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ORIGINAL PAPER

The influence of phosphonic acid pretreatment on the bronze corrosion protection by waterborne coating

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Abstract

This work examines the possibility of acrylic waterborne coating application in the protection of bronze cultural heritage. In order to enhance the coating protective properties, the surface pretreatment with long-chain phosphonic acid is investigated. Studies are conducted on bronze, either bare or covered by two types of patina, by using polarization measurements and electrochemical impedance spectroscopy during 3 weeks of continuous immersion in simulated urban acid rain solution. The role of 12-aminododecylphosphonic acid as corrosion inhibitor and adhesion promoter is studied. The results obtained within this research show that the corrosion protection by the waterborne coating increases in time in all cases and it is enhanced by the phosphonic acid pretreatment. The greatest impact of studied pretreatment on the overall corrosion protection level is observed on bare bronze substrate.

Keywords Bronze · Corrosion protection · Patina · Phosphonic acid · Waterborne coating

Introduction

Bronze cultural heritage, placed outdoors, is susceptible to deterioration caused by the presence of moisture and air pollution. Under the influence of aggressive compounds, bronze begins to corrode and cover itself with a layer of corrosion products called patina. The conservation profession uses different methods of corrosion protection for both bare and patinated bronzes. Preservation of patina is important as the patina has both an aesthetic and protective value. The most common method of protection is the application of acrylic varnish (mainly family Paraloid), although its photooxidation can be observed over time, eventually leading to yellowing and degradation [1–4]. Waxes and corrosion inhibitors are also used; however, some of the common corrosion inhibitors, like benzotriazole, pose a toxicity problem [1, 2, 5]. The varnishes, used nowadays, contain organic solvents that evaporate during varnish application and drying, which raises environmental and health issues. For this reason, there is a growing interest in the development of more environmentally friendly coatings, such as the waterborne coatings.

So far, corrosion protection by various waterborne coatings has been investigated but mostly on steel substrates. Unfortunately, their application brings problems such as poor surface wetting, corrosion of the metal substrate, and a lower level of protection compared to solvent-based coatings [6–9]. Various approaches were taken in order to overcome these problems. Zhong et al. proposed the use of silicone-modified polymeric coating, which they investigated for stainless steel corrosion protection [6]. They found that the incorporation of nanosilica particles into latex films could directly increase the thermal stability and mechanical properties of the coating as well as the corrosion resistance performance. Other approaches included the use of fluoropolymers due to their superior hydrophobicity. Wang et al. [10] prepared waterborne polyurethane coating modified with fluorinated acrylate that showed improved level of protection for carbon steel, compared to commercial water-based fluorocarbon resin—fluoro-olefine vinyl ether (FEVE) copolymer. This was attributed to surface hydrophobicity caused by the migration of long fluorine side chains during the curing process as well as to internal dual cross-linking that prevented the rapid penetration of water molecules. Still, the decrease in corrosion protection level occurred in both cases upon the longer exposure to corrosive medium [10].

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FEVE compounds were also developed by Mihelčič et al. [8] for the preparation of, both organic solvent and water-based, coating for bronze corrosion protection in chloride solution; again, the organic solvent-based coating showed higher protection. Swartz et al. [9] attempted to protect bronze from corrosion with a waterborne latex dispersion containing polyacrylics and poly(vinylidene fluoride) (PVDF). Due to low adhesiveness of PVDF coatings, researchers combined it with the organic coating—Paraloid B-44—to achieve satisfactory protection, but the surface whitening was observed in time due to the migration of coalescing agent. Considering that fluorinate compounds are expensive, the fluorinate modification is expensive as well a complex process. In their work, the use of adhesion promoters was proposed as the solution for the use of purely water-based coating systems.

Many researchers have studied various improvements of waterborne acrylic coatings by applying corrosion inhibitors and/or nanoparticles. For instance, Ress et al. doped pH sensitive colophony microcapsules containing corrosion inhibitor which provided better corrosion protection for carbon steel from chloride attack [11]. González et al. incorporated CeO_2 nanoparticles into metal coating binder as corrosion inhibitor contributing to higher coating barrier properties on steel substrates [12]. The enhancement of the steel corrosion protection by waterborne acrylic coating with cerium oxide nanoparticles was confirmed by Ecco et al. [13]. Other approaches included the addition of carbon nanotubes, which had a positive effect on the adhesion strength and corrosion protection of carbon steel [14]. Another example is alkyd–based waterborne coating modified with nanoalumina. Well-dispersed nano-Al_2O_3 particles acted as a barrier to electrolyte penetration in mild steel, providing a more stable coating [15].

In addition to acrylic coatings, waterborne epoxy coatings have also been investigated [16]. They also can be modified by fluorinating components [17] or the addition of inhibitor [18]. However, epoxy coatings are irreversible, which limits their application for the protection of cultural heritage [1].

Corrosion protection can be improved also by using sol–gel coatings. Effective copper and bronze protection in acid rain or chloride ion–containing solution was achieved by 3-mercapto-propyl-trimetoxy-silane (PropS-SH) coating [19, 20]. Furthermore, 3-mercapto-propil-trimetoxysilane improved the corrosion protection of an artificial sulphide patina on Cu-Si-Mn bronze exposed to artificial acid rain. It proved to be more protective than Incralac, a varnish normally applied to the outdoor artistic bronzes [21]. Silane pretreatment also enhanced barrier properties for copper/silane/epoxy coating [22]. In general, organosilane molecules can be used as adhesion promoters and for corrosion protection improvement [23–25].

Various approaches in protection of copper and its alloys also include protective films of different types of organic corrosion inhibitors, such as azoles [26, 27], leather black dye [28], or long-chain organic acids [29, 30]. For example Elia et al. [31] examined corrosion protection of copper by electrochemically deposited copper carboxylate layer. However, only tenfold decrease of copper corrosion current rate was observed. Our recent research showed that long-chain phosphonic acids efficiently protect copper-nickel alloys [29] and bronze surfaces [30]. They form self-assembled monolayers that bond to the metal surface, forming a stable protective film and limiting the diffusion of corrosive medium, resulting in a reduction of corrosion rate. However, thin films of phosphonic acids are not sufficient for a long-term protection in an aggressive environment. Still, several studies have shown that the phosphonic acids can enhance corrosion protection efficiency of organic or inorganic coatings. For example the addition of aminotrimethylene phosphonic acid (ATMP) during the production of a silica-based coating was found to improve the protection of aluminium alloy [32]. This behaviour was attributed to the strong chemical bonding of phosphonate groups to the aluminium substrate. Phosphonic acids were also found to improve the adhesion and corrosion resistance of epoxy resin on copper [33], as well as the corrosion protection of patinated bronze by Paraloid B-72 [34].

To our knowledge, there are so far no studies examining the influence of phosphonic acids on waterborne coatings' protective properties. As the cultural heritage is mainly protected by solvent-based acrylic coatings, it is interesting to examine their waterborne counterpart [35]. Waterborne polyacrylate (WPA) exhibits excellent properties in terms of hardness, weather ability, and chemical resistance [10, 36, 37], but the problem of lower corrosion protection level and possible substrate corrosion has to be solved. Therefore, in this work, the phosphonic acid pretreatment was examined as a modification strategy for the improvement of corrosion protection of bare and patinated bronze by waterborne acrylic coating. Long-chain phosphonic acid can act as corrosion inhibitor that could decrease the bronze and patina dissolution in the pores of the coating exposed to corrosive environment as well as during the coating application, when surface is in contact with water. In addition, its role as adhesion promoter was examined as well.

Very few studies with waterborne coatings have been conducted on bare bronze and even less on bronze covered by patina layer, which is a common case in bronze cultural heritage conservation. Studies in this work were performed on bare bronze and two kinds of patinated bronze surfaces, sulphide patina and electrochemically modified sulphide patina. In common practise, artificial patination of bronze sculptures is often carried out with a sulphide solution, resulting in the formation of a dark or brown patina, which simulates aged bronze covered by a layer of CuO [38]. During further aging of bronze and patina in urban outdoor environment, an additional green or bluish layer of patina is formed, consisting mainly of copper carbonates or sulphates. Chemical or electrochemical patination can be used to simulate such processes in a laboratory [39–43]. Corrosion protection of bare and patinated bronze by waterborne acrylic coating was studied by polarization measurements and electrochemical impedance spectroscopy conducted during continuous immersion in simulated urban acid rain (pH 5), which mimicked the corrosive urban environment. It is important that the coating does not change the appearance and composition of the bronze and patina it covers. Therefore, the attention was also focused on the visual appearance of the bronze and patina during application of the coating. That is another reason why the application of waterborne coatings in the protection of cultural heritage presents a particular challenge. In addition, the adhesion strength of the coating was determined by a pull-off test.

Experimental

Sample preparation

Experiments were performed on CuSn12 bronze (Cu 87.94%, Sn 11.02%, Zn 0.07%, Pb 0.54%), received from Strojopromet Ltd., Zagreb, Croatia. The bronze rod was cut into 0.5-cm-thick discs with upper surface 1.33 cm^2, a copper wire was soldered to the back of the discs, and they were embedded into an epoxy resin in order to serve as working electrodes for electrochemical measurements. The **bronze** samples were polished with 80, 800, 1200, 2500, and 4000-grade SiC paper; afterwards, they were degreased in an ultrasonic bath with ethanol and rinsed with deionized water.

To obtain chemical **sulphide patina**, the bronze samples were preheated to 80 °C. The hot samples were immersed in K_2S_n solution (0.1 g/50-mL distilled water) heated to 80 °C for 2 min [44]. Afterwards, the samples were washed with tap water and gently polished with paper in order to remove loosely attached patina. Such formed patina was adequately stable, so only one application was sufficient. After the preparation, samples were dried for 2 days at room temperature before further examination. The **electrochemical patina** was formed on sulphide bronze substrates. Six electrodes were connected in parallel and immersed in an artificial rainwater with pH ~ 8 (0.2 g/L Na_2SO_4, 0.2 g/L $NaHCO_3$, and 0.2 g/L $NaNO_3$ in redistilled water) [39]. Graphite was used as the counter electrode and a saturated calomel electrode as the reference. After a stable open circuit potential (E_{OCP}) was reached, anodic polarization, under potential control, was conducted:

1. At + 0.120 V vs. E_{OCP} during 5 h
2. At + 0.100 V vs. E_{OCP} during next 17 h
3. At + 0.110 V vs. E_{OCP} during another 32 h
4. At + 0.95 V vs. E_{OCP} during another 14 h
5. At + 0.110 V vs. E_{OCP} during last 30 h

Protective coating application

Phosphonic acid pretreatment was conducted on part of the samples by using 12-aminododecylphosphonic acid hydrochloride (12-amino, 95%), obtained from Alfa Aesar, Germany. For the bare bronze, the treatment included four steps. The first step was an oxide layer formation in an air convection oven for 24 h at 80 °C. The second step was the adsorption of 12-amino acid on the oxidised surface from a 10^{-4} M ethanolic solution (ethanol 96% p.a. obtained from LabExpert d.o.o., Croatia). The samples were immersed in the solution for 4 h at 40 °C. After drying at 80 °C for 3 h, bronze surface was gently wiped with lens paper soaked in ethanol and placed in an ultrasonic bath for 10 min to remove unstable multilayers. Finally, the samples were additionally dried at 80 °C for 1 h. The procedure for acid adsorption was developed following the study by Kristan Mioč et al. [29].

In order to create a protective system for patinated bronze samples, 12-amino acid solution was applied by brush five times every 15 min and dried at 80 °C for 5 h before coating application. For patinated samples, it was not possible to use immersion application, described for bare bronze, as it resulted in patina color alternation.

The waterborne acrylic coating used is still a noncommercial product obtained from a paint producing company. It was applied with a brush three times every 24 h (each subsequent brush stroke is perpendicular to the previous one), cured at 40 °C for 4 h after each application, and stabilised for 10 days before exposure to the artificial acid rainwater. Coating was applied by the same procedure onto the samples with (**12-amino/coating**) or without (**coating**) phosphonic acid pretreatment. The dry film thickness on all samples was 16 ± 5 µm. Figure 1 presents an overview of sample preparation and coating application procedure.

Electrochemical investigations

The corrosion protection of bare and patinated bronze was examined by electrochemical methods. Measurements were collected with Bio-Logic SP-300 potentiostat connected to the three-electrode electrochemical cell where examined bronze samples acted as working electrode, the graphite rod as the counter, and the saturated calomel electrode as the reference electrode. Artificial acid rainwater (0.2 g/L Na_2SO_4, 0.2 g/L $NaHCO_3$, and 0.2 g/L $NaNO_3$ in redistilled water) with pH 5, adjusted with 0.5 M H_2SO_4, served as the electrolyte solution.

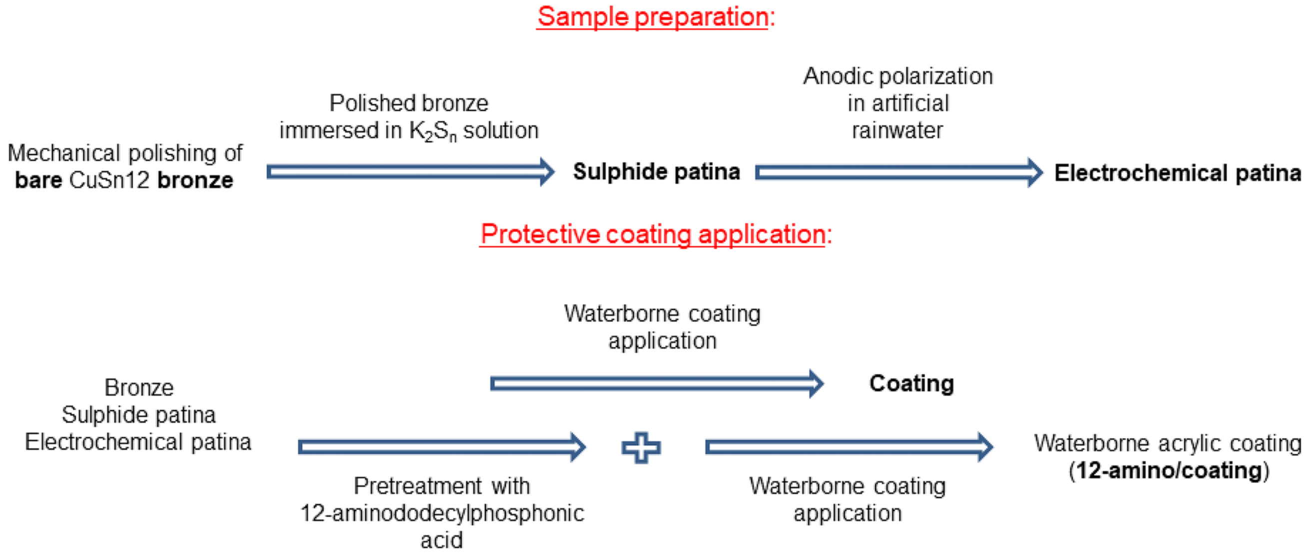

Fig. 1 Schematic representation of sample preparation and coating application procedure (in bold letters is designation of samples which is used later in the text)

Measurements were performed after potential stabilisation during 45 min in order to avoid a change of open circuit potential (E_{OCP}) during the measurement.

Potentiodynamic polarization measurements were performed in a wide (± 150 mV vs. E_{OCP}) potential range at scan rate 0.166 mV s^{-1}. Additional set of samples was continuously exposed to artificial acid rainwater for 22 days. On these samples, periodical electrochemical measurements were performed, potentiodynamic polarization in a narrow (± 25 mV vs. E_{OCP}) potential range, followed by electrochemical impedance spectroscopy (EIS) measurements, which were conducted at E_{OCP} in the frequency range of 100 kHz–10 mHz with an amplitude of 10 mV.

Adhesion strength measurement

Coating adhesion was investigated by pull-off test using a PosiTest® AT, DeFelsko. It was performed on 5 × 5-cm bronze plates with a thickness of 5 mm. The measurements were performed on bare and sulphide patinated bronze protected by both waterborne acrylic coating and waterborne acrylic coating modified with 12-aminododecylphosphonic acid hydrochloride. On each surface, 4 dollies were glued by the two-component epoxy adhesive. The dollies were positioned perpendicular to the surface, avoiding the edge of the plate. After 24 h of drying, they were pulled off, measuring the maximum adhesive strength of the coating.

Results and discussion

Potentiodynamic polarization investigations on influence of phosphonic acid pretreatment on corrosion protection was conducted in a wider and narrow potential range in order to compare the corrosion resistance of bare samples and those protected either with only a waterborne coating or with protective system 12-amino acid/waterborne coating. Measurements in the wider potential range were conducted after 45 min of immersion in order to evaluate the protection level, while the measurements in the narrow potential range were conducted during 3 week period in order to follow the coating behaviour and durability in acid rain solution.

Initial protection evaluation

The influence of acid pretreatment on the corrosion protection of bare and patinated bronze was investigated by polarization in a wide potential range. All measurements were carried out in artificial acid rain solution (pH 5). The strong decrease in cathodic and anodic current densities, indicating an improvement in corrosion resistance, was observed for all studied bronze surfaces protected by waterborne coating, (Fig. 2). Protection by waterborne coating (with or without 12-amino acid treatment) caused the shifts of the corrosion potential towards negative direction which is

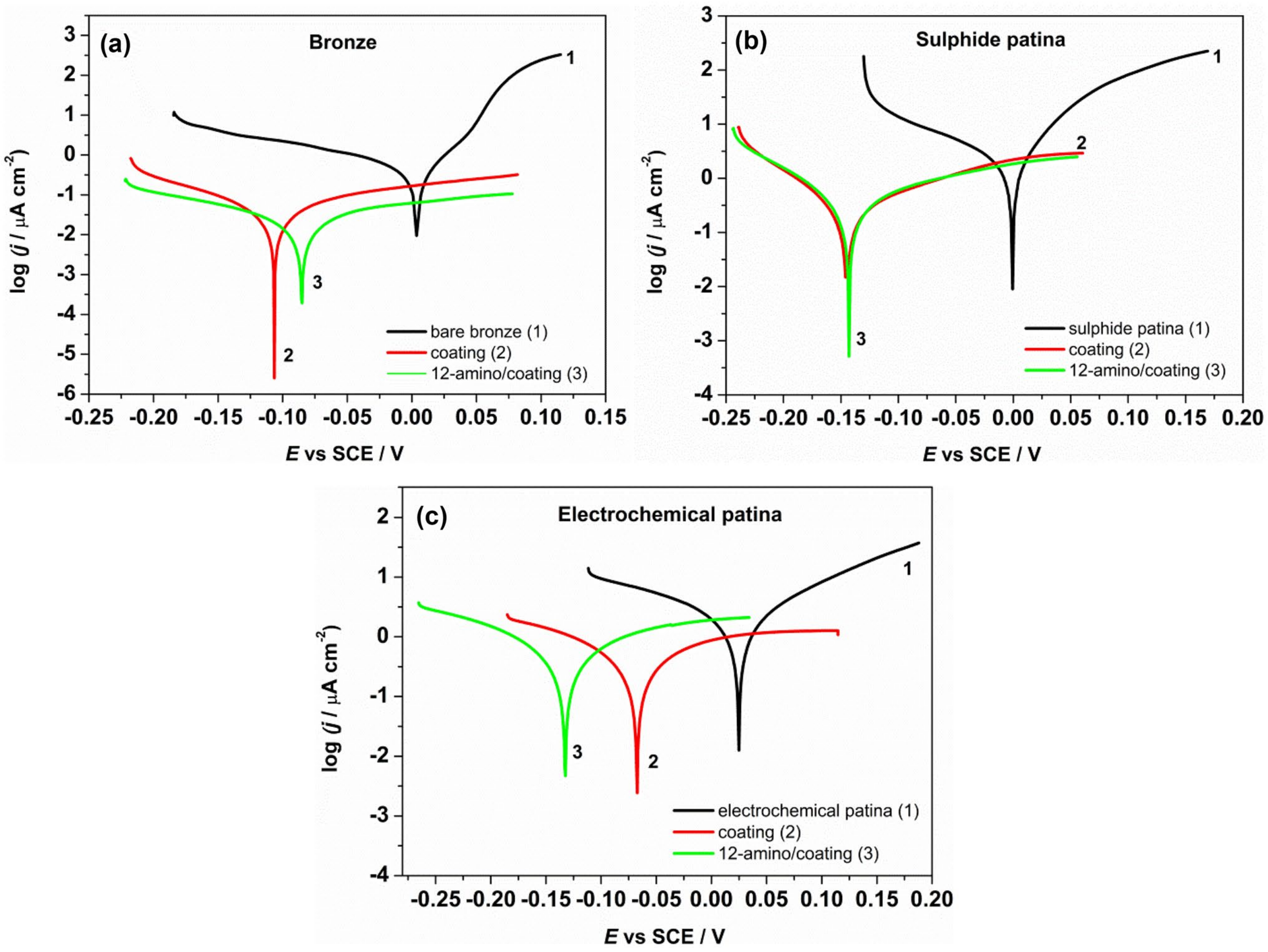

Fig. 2 Polarization curves of **a** bare, **b** sulphide patinated, and **c** electrochemically patinated bronze in acid rain (pH 5)

usually explained by a stronger decrease in cathodic reaction rate compared to the decrease in anodic reaction rate. In the case of bare bronze, cathodic and anodic current densities of coated samples were lower for two orders of magnitude, while for patinated samples, a decrease in current densities was in a range of one order of magnitude. In studies with solvent-borne coatings, a much stronger suppression of current densities is expected but studies with waterborne coatings often lead to similar results. For example studies on bare bronze in 0.5 M NaCl showed that waterborne fluoropolymer coating decreased only anodic current densities for two orders of magnitude while cathodic currents remained similar to unprotected sample [8]. Similarly, protection of steel in 0.5 M NaCl by waterborne acrylic coating doped with inhibitors resulted in only one order of magnitude lower current densities [11].

The phosphonic acid pretreatment appeared to have the most significant influence on protection of bare bronze (Fig. 2a), among the studied substrates. The shift of polarization curve of the pretreated and coated bronze sample towards lower current densities, compared to coated-only sample, is clearly observed. The beneficial effect of phosphonic acid pretreatment reflects also in lower corrosion current densities as can be observed from corrosion parameters presented in Table 1. They were obtained from polarization curves by Tafel extrapolation method although in the case of the coated samples, an increase in anodic Tafel slopes points towards the fact that anodic reaction was probably under mixed diffusion and activation control. For that reason, obtained corrosion current densities (j_{corr}) should be observed as an approximation.

The corrosion parameters (Table 1) show that for both kinds of unprotected patinated bronzes, the corrosion current density is higher than for bare bronze. This could be explained by the higher reactivity of the patinated substrates, especially sulphides, which may also contribute to the increased corrosion of the metal surface. Reactivity of the patina may be also caused by the short stabilisation time

Table 1 Corrosion parameters for different substrates obtained by the Tafel extrapolation method. The values in parenthesis represent standard deviations

	E_{corr} (mV vs. SCE)	j_{corr} (μA·cm^{-2})	β_a (mV·dec^{-1})	$-\beta_c$ (mV·dec^{-1})
Bronze				
Bare	− 26 (27)	1.03 (0.62)	34 (1)	81 (16)
Coating	− 93 (11)	0.04 (0.01)	76 (7)	75 (6)
12-Amino/coating	− 92 (7)	0.03 (0.01)	76 (1)	74 (5)
Sulphide patina				
Bare	− 18 (15)	1.61 (0.38)	40 (6)	91 (13)
Coating	− 82 (90)	0.39 (0.21)	78 (28)	72 (18)
12-Amino/coating	− 131 (17)	0.45 (0.33)	70 (0)	49 (4)
Electrochemical patina				
Bare	24 (5)	1.73 (0.64)	61 (24)	76 (7)
Coating	− 57 (16)	0.25 (0)	78 (9)	81 (11)
12-Amino/coating	− 90 (38)	0.34 (0.28)	83 (14)	80 (3)

after patina preparation [38], as well as by increased surface area compared to bare bronze surface. Figure 2b shows the polarization curves for sulphide patina substrates while the polarization curves for electrochemical patina are shown in Fig. 2c. For the electrochemical patina and sulphide patina, phosphonic acid pretreatment did not have a beneficial effect on the corrosion protection of waterborne coating which can be related to their higher reactivity. The phosphonic acid pretreatment of electrochemically patinated bronze slightly increased the anodic current densities and shifted the corrosion potential towards more negative direction. In general, anodic Tafel slopes for all unprotected samples are lower than the corresponding cathodic Tafel slopes, which implies cathodic control of the corrosion rate. On the other hand, for protected samples, the values of anodic and cathodic Tafel slopes are quite similar, such that the mixed control of corrosion rate can be proposed. The only exemption is 12-amino/coating system on sulphide patina exhibiting anodic control of the corrosion rate. The possible explanation of such exemption could be in additional cathodic reaction involving reduction of copper ions from 12-amino acid complex with sulphide patina. The summary results of the Tafel extrapolation for bare bronze, sulphide, and electrochemical patina are shown in Table 1, respectively.

Linear polarization

Polarization measurements were also conducted in a narrow potential range by linear polarization. In this way, it was possible to determine the polarization resistance (R_p), i.e., corrosion resistance of studied samples over longer period. The results obtained are shown in Fig. 3.

Results presented in Fig. 3a confirm the previous findings that waterborne coating improved the corrosion resistance of bare bronze, as well that the phosphonic acid pretreatment additionally increased the corrosion protection level. Samples pretreated with 12-amino acid, before waterborne coating application, exhibited superior corrosion resistance during the whole period of exposure to artificial acid rainwater. It is also interesting to notice that the R_p of coated samples increased with immersion time which is not something typically seen for metals covered by organic coatings. In contrast, it is usually observed that the corrosion protection decreases in time as water penetrates into the coating. Similar issue was examined by Le Pen et al. [45] for water-based epoxy coatings. They have found that such behaviour can be attributed to a coalescence of the polymer particles in water-based film, which is a process accelerated by the coating immersion in the aggressive solution. The drying of waterborne coatings is much slower than that of the solvent-borne coatings and consist of three steps where the last one is the coalescence stage, which can take a long time, several days or even weeks if the sample is dried at room temperature [9, 35, 45]. It can be assumed that in our study, coating coalescence was not completed during the drying step and was accelerated when the sample was immersed in the acid rain solution.

The results for sulphide patina and electrochemical patina are presented in Fig. 3b, c, respectively. Initially, the difference in polarization resistance between coated and unprotected samples is not as significant as in the case of the bare bronze. The less efficient corrosion protection of patinated bronzes can be attributed to the difference in substrate, as patinated surfaces are more reactive, rougher, and porous compared to bare bronze surface. Thus, it is possible that during the coating application, patina was partially dissolved and then precipitated in the pores of the coating, which resulted in lower efficiency of corrosion protection. However, R_p of all coated samples (either pretreated or not) significantly increased in time. On the sulphide patina substrates, these values become similar to those obtained on bare bronze, while the R_p values of coated electrochemical patina were one order of magnitude lower. Taking into account that electrochemical patina was formed over sulphide patina and that such patina layer

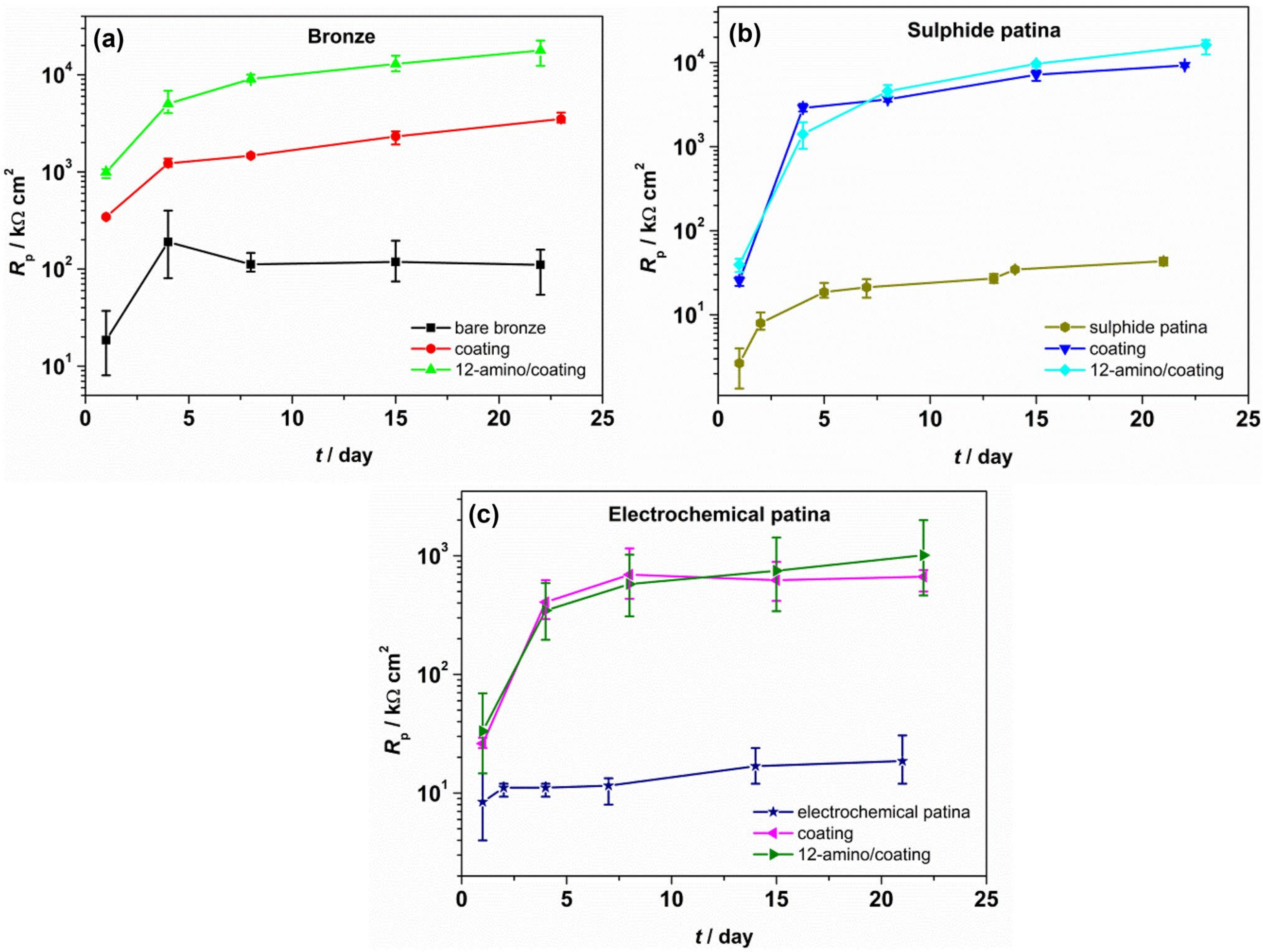

Fig. 3 Dependence of polarization resistance R_p on immersion time in acid rain solution (pH 5) for **a** bare, **b** sulphide patinated, and **c** electrochemically patinated bronze

was thicker and rougher, it may be also assumed that such behaviour is related to the amount of the patina present in the coating. However, this aspect will be further examined by the means of electrochemical impedance spectroscopy.

When examining the influence of 12-amino acid pretreatment, it is clear that for both patinated substrates during the first few days of immersion, the difference between pretreated and coated-only samples was not significant. However, upon the longer exposure to artificial acid rainwater, pretreated samples exhibited higher corrosion resistance than just coated samples.

Corrosion behaviour examined by electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy is a useful technique for more detailed analysis of coating protecting mechanism. Impedance spectra obtained on bare bronze, protected with either coating alone or in combination with 12-amino acid, are presented in Fig. 4. EIS spectra clearly show that the impedance of both types of protected samples increased in time but 12-amino pretreated samples always exhibited superior corrosion resistance, which is in accordance with the results of the polarization measurements (Fig. 3). When examining the phase angle plot, two maxima can be observed, corresponding to two time constants. In general, EIS spectra of highly protective solvent-based coatings are characterized with wide phase angle maximum close to − 90° as only the impedance of the coating is visible in the spectrum [46–49]. When water reaches the surface of metal, corrosion starts and the second phase angle maximum is then observed [46–53]. In the case of waterborne coatings, that in principle exhibit inferior corrosion protection compared to solvent-borne coatings, it is not uncommon to observe two phase angle maxima already on freshly applied coatings, as is the case in this work. Such spectra typically can be modelled with equivalent electrical circuit presented in Fig. 5a consisting of the *R*-*Q* couple describing

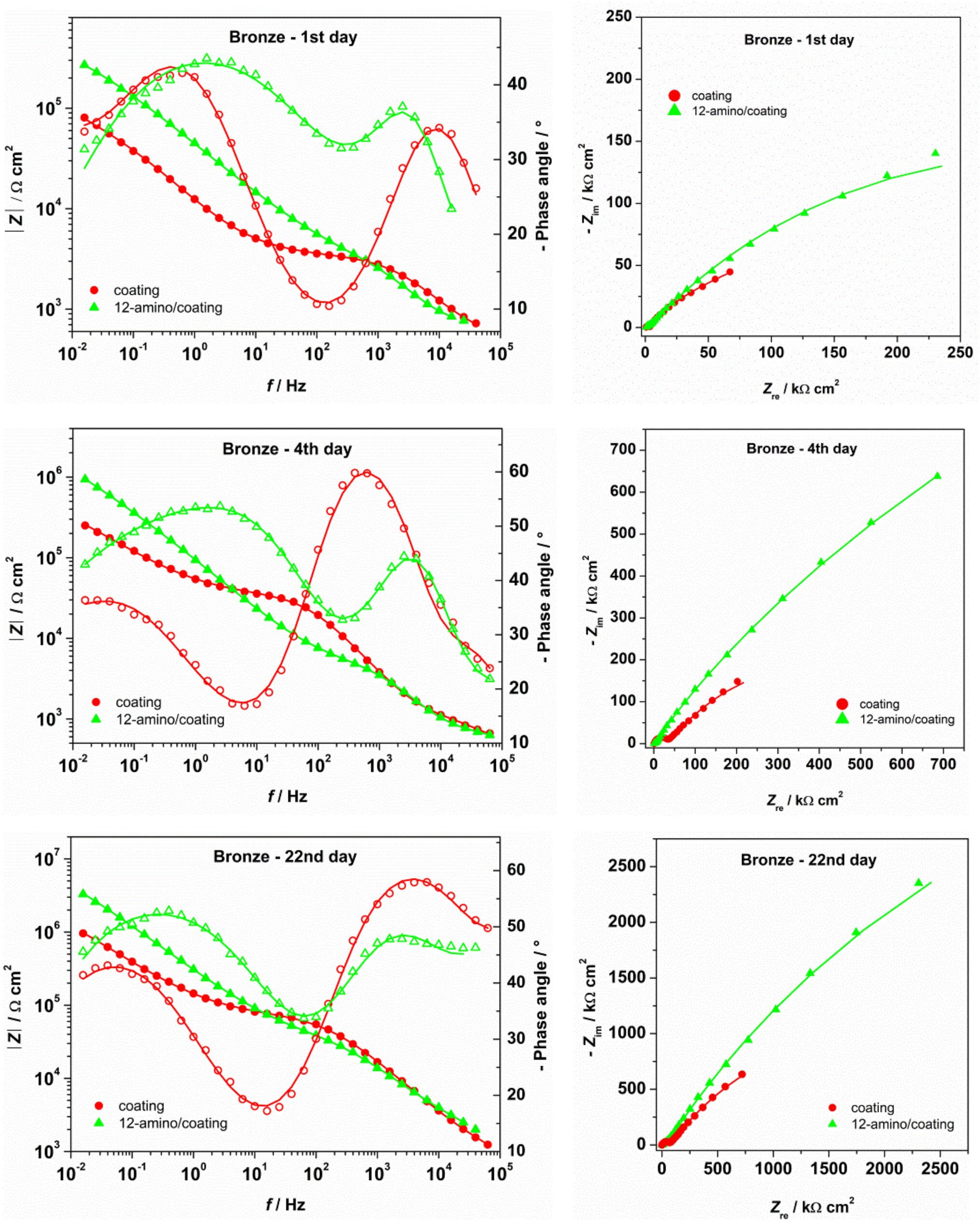

Fig. 4 EIS spectra for bare bronze during 3-week exposure to acid rain (pH 5). Left side—Bode plot; solid symbols—impedance; open symbols—phase angle; right side—Nyquist plot. In all graphs, symbols represent experimental data and lines represent fitted data

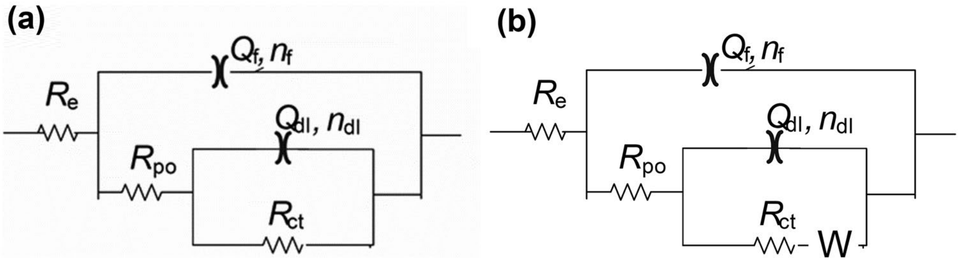

Fig. 5 Electrical equivalent circuits with **a** two time constants and **b** additional Warburg diffusion element for analysis of EIS data (R_{po} resistance of pores in the coating; Q_f constant phase element representing the coating capacitance; R_{ct} charge transfer resistance; Q_{dl} constant phase element describing the double-layer capacitance; n_f and n_{dl} nonideal capacitive behaviour)

the behaviour of coating (R_{po} resistance of pores in the coating and Q_f constant phase element representing the coating capacitance) and R-Q couple representing the corrosion process on metal surface (R_{ct} charge transfer resistance and Q_{dl} constant phase element describing the double-layer capacitance). Coefficients n_f and n_{dl} describe the nonideal capacitive behaviour [17, 25, 46–51]. For coated-only sample spectra (1st and 4th day), it was found that in order to achieve the good fitting of EIS spectra, it was necessary to introduce the additional Warburg diffusion element as presented in Fig. 5b [10].

From Table 2, it is evident that for both coating systems, coating resistance increased in time followed by the slight decrease in coating capacitance. As mentioned before, Le Pen et al. [45] observed the increase in pore resistance of waterborne coating during the first days of immersion which was attributed to coalescence process, but in their case, the increase of coating capacitance was observed due to the ingress of water into the coating. On the other hand, Ecco et al. have observed by EIS studies on waterborne coatings on mild steel both increase in impedance and decrease in coating capacitance within the first 24 h of immersion [54]. AFM studies revealed that such behaviour can be attributed to swelling of the coating due to the water uptake and closure of the pores in the coating. A similar mechanism can be proposed for the studied systems. As both coating and charge transfer resistances increased in time accompanied with the decrease in the value of coating and double-layer capacitive elements, it may be assumed that ingress of the water into coating resulted in pore closure due to the changes in coating structure, thereby decreasing the transport of water towards the metal surface and thus reducing the corrosion of the substrate. When examining the influence of amino acid pretreatment, it is clear that pretreated samples exhibited higher R_{ct} and lower Q_{dl} values compared to coated-only samples, which confirms phosphonic acid adsorption on bronze surface and its behaviour as corrosion inhibitor. On the other hand, R_{po} was initially similar for both systems while the Q_f value was even lower for pretreated samples. The possible explanation would be that 12-amino phosphonic acid molecules were present not only at the bronze surface but also in the pores of the coating, thereby preventing the water diffusion and slowing down the coating coalescence process.

EIS spectra for bronze substrates covered by sulphide patina layer and protected with studied coatings are presented in Fig. 6. The obtained spectra confirm that 12-amino acid pretreatment had beneficial effect on coating corrosion protection except for the fourth day of immersion (as was also observed from R_p measurements). In contrast to spectra obtained on bare bronze, these spectra exhibit three time constants. Our previous study on corrosion behaviour of sulphide patinated bronze [38] pointed out the high reactivity of such patinated surface; thus, it is plausible to assume that the third time constant corresponds to oxidation/reduction reactions involving patina reactive compounds (R_F-Q_F) as previously described by Evesque et al. for silver coated with thiol layer [55]. Faradaic impedance of reactive patina compounds was described in details by Marušić et al. [56]. The electrical equivalent circuit used for modelling of these spectra is given in Fig. 7a. In the case of coated sample 1st

Table 2 EIS data for bare bronze during 3-week exposure to acid rain (pH 5)

Bronze		R_{po} (kΩ cm^2)	Q_f (μS s^n cm^{-2})	n_f	R_{ct} (kΩ cm^2)	Q_{dl} (μS s^n cm^{-2})	n_{dl}
1st day	Coating	3.03	0.03	0.74	76.3	27.2	0.66
	12-Amino/coating	2.42	0.08	0.91	622	7.79	0.53
4th day	Coating	33.3	0.11	0.86	718	12.7	0.57
	12-Amino/coating	6.46	0.05	0.92	$6.33 \cdot 10^3$	1.79	0.71
22nd day	Coating	73.5	0.06	0.74	$4.16 \cdot 10^3$	3.62	0.60
	12-Amino/coating	44.6	0.05	0.75	$1.33 \cdot 10^4$	0.94	0.62

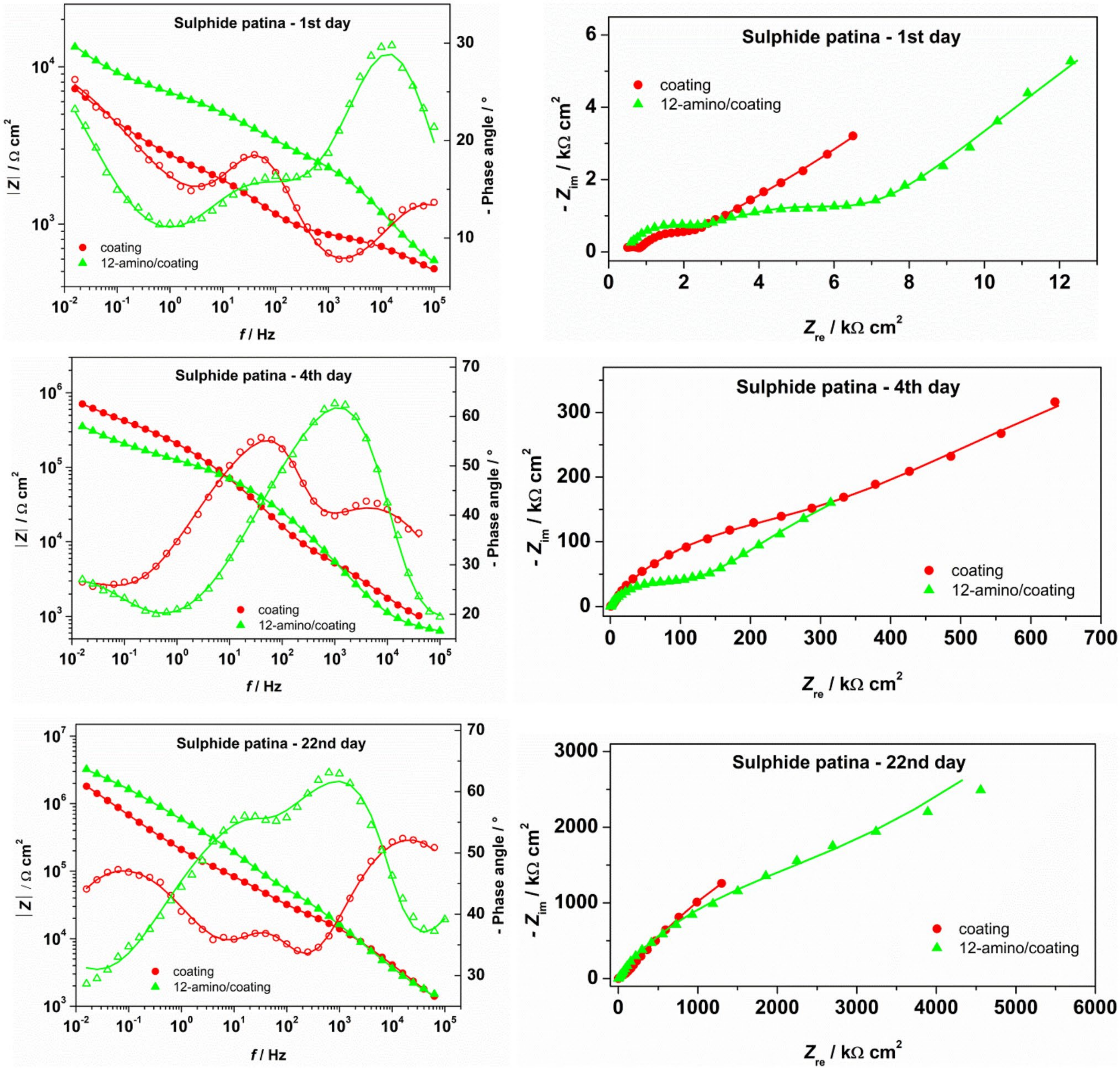

Fig. 6 EIS spectra for sulphide patina during 3-week exposure to acid rain (pH 5). Left side—Bode plot; solid symbols—impedance; open symbols—phase angle; right side—Nyquist plot. In all graphs, symbols represent experimental data and lines represent fitted data

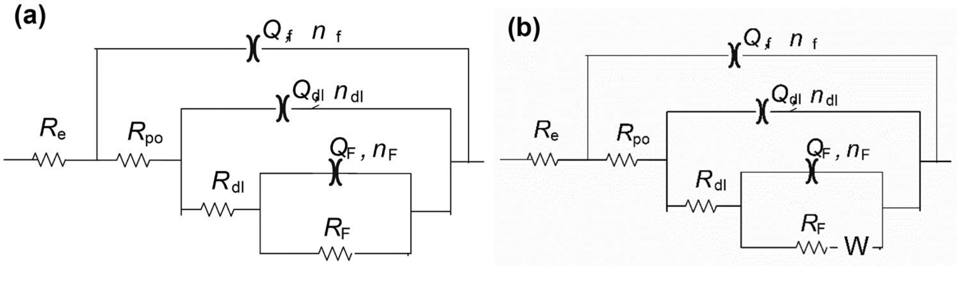

Fig. 7 Electrical equivalent circuits with **a** three time constants and **b** additional Warburg diffusion element for analysis of EIS data (R_{po} resistance of pores in the coating; Q_f constant phase element representing the coating capacitance; R_{ct} charge transfer resistance; Q_{dl} constant phase element describing the double-layer capacitance; R_F faradaic resistance of reactive patina layer; Q_F reactive patina capacitance; n_f, n_d, and n_F nonideal capacitive behaviour)

day and pretreated sample 22nd day, it was necessary to use additional Warburg diffusion element to obtain a good fit (Fig. 7b).

EIS parameters (Table 3) describing the coating properties showed similar behaviour to that observed on bare bronze, i.e. increase in pore resistance and decrease in coating capacitance in time. Similar trend was observed for the R_{ct}-Q_{dl} couple describing behaviour of bronze surface and for the R_F-Q_F couple describing the properties of reactive patina layer. Obtained results confirm improvement of coating barrier properties in time, although this improvement was less pronounced on pretreated samples. On the other hand, pretreated samples exhibited higher charge transfer resistance and patina layer resistance which can be related to the protective effect of 12-amino phosphonic acid, adsorbed both on the patina and bronze surface.

EIS studies on electrochemical patinated bronze (Fig. 8) also revealed the increase in impedance in time for both studied coating systems, as well as that pretreated samples exhibited higher impedance compared to coated-only samples. The shape of the impedance curves was somehow different than in the case of sulphide patina (Fig. 6). The phase angle maxima were observed at high and medium frequencies while at low frequencies, phase angle values were very low as the impedance spectra are very flattened. Figure 9c shows the image of electrochemically patinated surface covered by a coating; a part of the surface is uniformly covered by a dark sulphide patina while the other parts are covered by a thicker layer of bluish corrosion products. It was assumed that, similar to bare and sulphide patinated samples, high- and medium-frequency region of the EIS spectra represented coating response and corrosion of the substrate while the spectra in the low-frequency region resulted from this bluish patina layer. According to Levie's theory of porous electrodes [57, 58], the phase angle of the impedance of a porous electrode is half of that of the flat electrode. From Nyquist plots in Fig. 8, it appears that most of the spectra exhibit an angle close to 22.6° with respect to the real axis which is ascribed to diffusion in semi-infinite porous medium. For the purpose of this study, we have analysed only the high- and medium-frequency part of the spectra where capacitive behaviour was clearly observed by using the equivalent electrical circuit shown in Fig. 5a. A similar trend in corrosion parameters (Table 4) was observed as for other two substrates. Namely, the coating pore resistance increased in time followed by the increase of charge transfer resistance and decrease in values of both associated constant phase elements. Phosphonic acid pretreatment had beneficial effect on charge transfer resistance values (especially for the last day of immersion), confirming its inhibitory effect on this type of substrate as well.

From the results obtained in this work, it is clear that 12-amino phosphonic acid pretreatment had beneficial

Table 3 EIS data for sulphide patina during 3-week exposure to acid rain (pH 5)

Sulphide patina		R_{po} (kΩ cm^2)	Q_f (μS s^n cm^{-2})	n_f	R_{ct} (kΩ cm^2)	Q_{dl} (μS s^n cm^{-2})	n_{dl}	R_F (kΩ cm^2)	Q_F (μS s^n cm^{-2})	n_F
1st day	Coating	0.57	1.95	0.56	1.23	15.5	0.75	10.2	372	0.48
	12-Amino/coating	2.28	0.59	0.66	4.56	21.6	0.53	99.5	370	0.50
4th day	Coating	18.7	0.95	0.59	358	0.04	1.00	$2.17 \cdot 10^3$	5.19	0.50
	12-Amino/coating	0.93	1.15	0.47	156	0.04	0.91	$1.18 \cdot 10^3$	10.4	0.53
22nd day	Coating	32.1	0.15	0.66	78.7	0.21	0.83	$9.36 \cdot 10^3$	1.73	0.59
	12-Amino/coating	4.03	0.26	0.58	8.90	0.01	0.93	$1.09 \cdot 10^4$	0.01	1.00

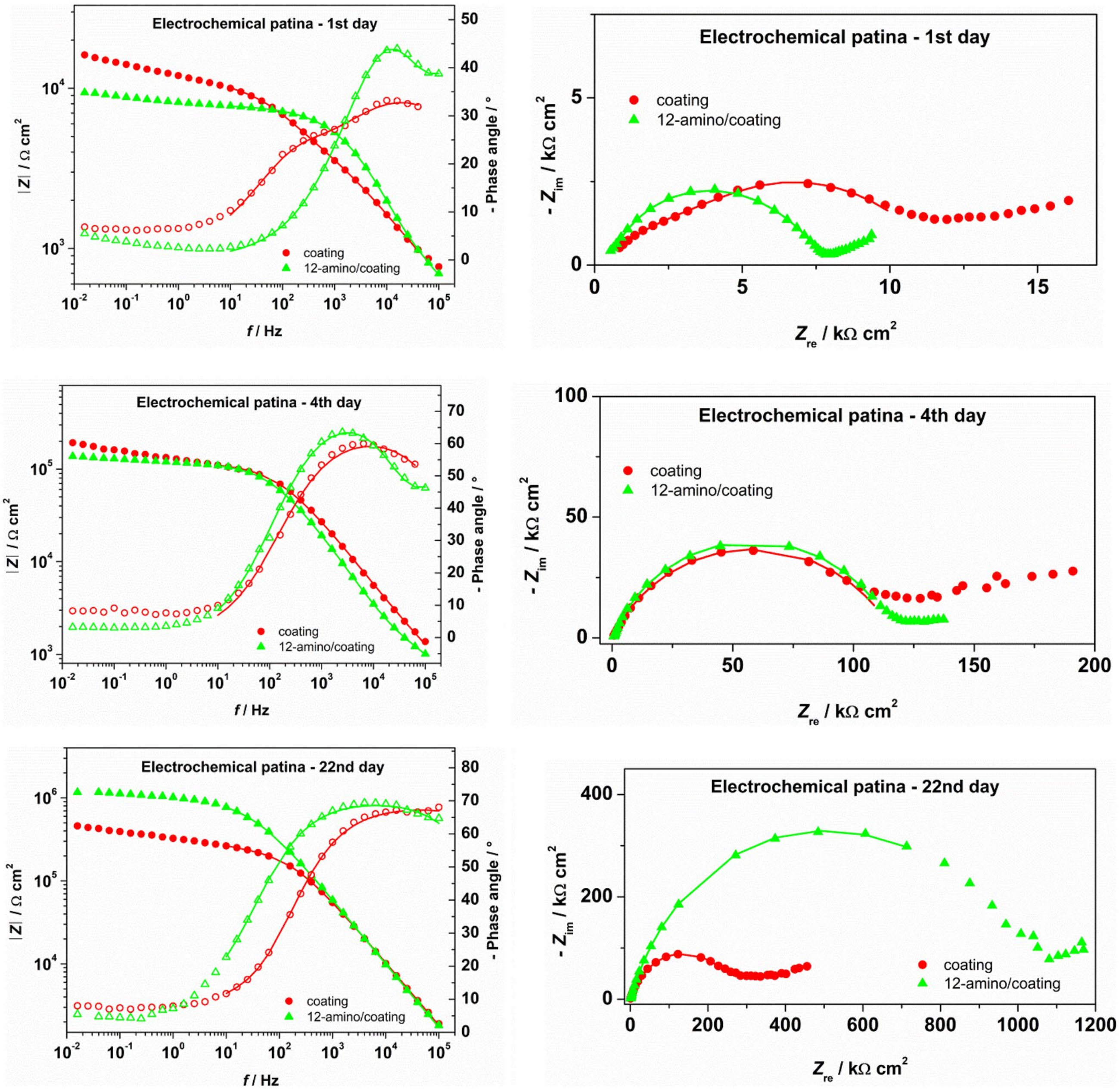

Fig. 8 EIS spectra for electrochemical patina during 3-week exposure to acid rain (pH 5). Left side—Bode plot; solid symbols—impedance; open symbols—phase angle; right side—Nyquist plot. In all graphs, symbols represent experimental data and lines represent fitted data

influence on corrosion protection of bare and patinated bronzes by protection of both bronze substrate and patina layer. The most significant effect of this pretreatment was observed on bare bronze compared to patinated bronzes which might be caused by the difference in phosphonic acid application, as well by the phosphonic acid film structure and compactness due to the differences in substrate morphology and composition. The compact, well-ordered film of phosphonic acid would more easily form on smooth bronze surface than on rough patinated surfaces. However,

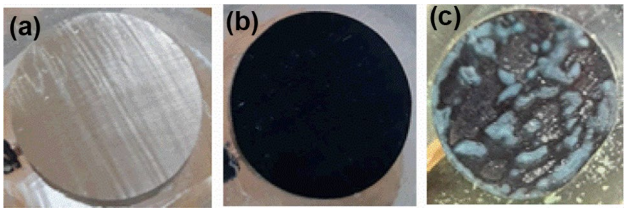

Fig. 9 Surfaces of pretreated and coated **a** bare, **b** sulphide patinated, and **c** electrochemically patinated bronze samples after exposure to acid rain for 3 weeks

Table 4 EIS data for electrochemical patina during 3-week exposure to acid rain (pH 5)

Electrochemical patina		R_{po} (kΩ cm^2)	Q_f (μS s^n cm^{-2})	n_f	R_{ct} (kΩ cm^2)	Q_{dl} (μS s^n cm^{-2})	n_{dl}
1st day	Coating	6.99	2.30	0.50	4.73	1.28	0.75
	12-Amino/coating	1.23	0.36	0.58	6.67	0.03	0.82
4th day	Coating	6.33	0.07	0.68	113	0.002	0.92
	12-Amino/coating	2.34	0.07	0.69	115	0.01	0.89
22nd day	Coating	257	0.02	0.76	65.9	0.63	0.83
	12-Amino/coating	766	0.02	0.78	353	0.33	0.51

measurements after prolonged exposure to corrosive medium showed superior corrosion resistance of pretreated patinated surfaces compared to coated-only surfaces. Thus, it is clear that in a long-term exposure, phosphonic acid pretreatment has a positive effect on waterborne coating corrosion protection efficiency.

In this study, we also focus on the visual appearance of the protected samples. Figure 9 shows studied surfaces protected by waterborne coating and phosphonic acid after being exposed to acid rain for 3 weeks. There were no visual differences between the sample appearance at the beginning of the immersion and after 3 weeks, as well as between the substrates protected with and without phosphonic acid.

Testing on coating adhesion by pull-off test

Phosphonic acids can act not only as corrosion inhibitors but also as adhesion promoters as it was described in the "Introduction" section. For that reason, coating adhesion was tested by pull-off method on bare bronze substrate (Table 5). The initial value of the adhesion strength of both coating systems was the same, regardless of the presence of phosphonic acid, reaching the values above 5 MPa. After a monthly exposure to acid rain (pH 5), pretreatment with phosphonic acid showed a strong effect on adhesion. In the case of waterborne coating, acid rain caused weakening of adhesion, which could be related to the penetration of the aggressive electrolyte to the bronze. These results confirm that 12-amino phosphonic acid acted as adhesion promoter, leading to an improvement in the interaction between the waterborne acrylic coating and the metal substrate.

These studies were also performed on patinated bronze, but during the investigation, the patina was peeled off due to its lower adhesion to substrate compared to the adhesion of coating on patina. Therefore, it was not possible to evaluate the adhesion of coating onto the patina layer.

Table 5 Pull-off test results of coating adhesion strength for bare bronze

Bare bronze	Before immersion (MPa)	After immersion (MPa)
Coating	5.4	2.6
12-Amino/coating	5.6	5.6

Conclusions

In this work, the possibility of bare and patinated bronze protection by waterborne acrylic coating was examined by the means of electrochemical methods. The obtained results show that for all studied substrates, the initially moderate barrier properties of the coating increased in time which was attributed to structural changes inside the coating when in contact with aqueous medium. Pretreatment of studied surfaces with 12-aminododecylphosphonic acid had a beneficial effect on their corrosion protection, especially in the case of bare bronze substrate. Electrochemical results confirmed that studied phosphonic acid formed a protective film on bronze and patina and decreased their dissolution in the pores of the coating. In addition, this pretreatment improved the adhesion of the waterborne acrylic coating exposed to artificial acid rainwater. From the obtained results, it is clear that protective system phosphonic acid/waterborne acrylic coating could be used for the protection of bare and patinated bronze surfaces.

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