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Protective effect of inhibitor-containing nitrocellulose lacquer on artificially patinated bronze

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ABSTRACT

In the present work, the efficiency and time-degradation of new protective organic coatings for artificially patinated bronze based on nitrocellulose lacquer containing thiadiazole derivatives (2-mercapto-5-amino-1,3,4-thiadiazole and 2-mercapto-5-methyl-1,3,4-thiadiazole) as corrosion inhibitors were investigated. The samples were intermittently exposed to a solution simulating an urban rain (pH 5) and their behaviour was monitored for nearly three months by electrochemical impedance spectroscopy (EIS) measurements.

Optical microscopy examination of cross sections of bronze samples covered with patina and nitrocellulose lacquer, without and with inhibitors, was used to determine the thickness of the coatings. Fourier transformed infrared spectroscopy (FT-IR) was employed to put on evidence the chemical interactions between the organic inhibitors and nitrocellulose lacquer functional groups.

The best results were achieved in the presence of 2-mercapto-5-amino-1,3,4-thiadiazole into the nitrocellulose lacquer coating, which offers the highest long-lasting protection to patinated bronzes, without changing the visual appearance of the bronze surfaces covered with patina. This approach proved to be a promising alternative to benzotriazole in the development of highly protective coatings for patinated bronzes.

1. Introduction

The natural (noble) patina observed on outdoor historical and artistic bronzes, or on archaeological artefacts exposed in museums, is formed spontaneously during long time exposure in the surrounding environment. Natural patina offers aesthetic and historical value to bronzes being associated to the authenticity of ancient objects [1–8]. The composition of the patina is part of the history of the object and, in some cases, conserves important information about the original shape, decoration or manufacturing techniques [9]. The noble patina also exerts some self-protecting effect towards the metallic substrate allowing its preservation [10]. Therefore, the protection and conservation of the patina covering the historical and artistic bronzes is one of the main concerns within the conservation practice, because if the patina is damaged, the corrosion processes could restart even more aggressively under the influence of the environment.

The procedure regularly used by conservators for the protection of bronzes covered with patina consists in the application of various coatings, using the least possible intrusive methods in the attempt to preserve the appearance of the original substrate. Thus, the ideal coating should be transparent, capable of providing efficient long-time protection, easily to apply and should have a viable, but safe removal method if it starts failing [9]. Another important aspect when proposing new corrosion protection methods for cultural heritage objects is the fact that, due to their unique nature and value, the evaluation of the efficiency of applied procedures cannot be made by direct measurements on historical objects, which could be irreversibly harmed, but only on samples of similar non-archaeological materials covered with artificial patina.

Nowadays, the most commonly used coating materials for the protection of the historic/artwork bronzes include acrylic resins (*i.e.* Incralac®, Paraloid B72®, Paraloid B44®) [9,11,12], cellulose nitrate [13], and natural, synthetic or microcrystalline waxes [14], with or

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without corrosion inhibitors. Usually, the addition of an organic inhibitor to the coating material offers an enhanced corrosion resistance and this combination is often used in the conservation treatments. Actually, many commercial products used for the protection of copper and its alloys already contain corrosion inhibitors. For instance, Incralac® is a solution of methyl-methacrylate/ethyl-methylacrylate dissolved in toluene, which contains epoxidized soya bean oil as a levelling agent and benzotriazole (BTA) as a corrosion inhibitor and UV-stabilizer [15]. Another commercial product containing BTA is Soter®, a mixture of crystalline wax and synthetic organic polymer, dispersed in turpentine and ether [16,17].

In spite of its extensive use in the conservation field, the stabilization of copper and bronze artefacts with BTA is not always successful; the treatment might change the visual appearance (colour) of the patina layer, especially in repeated applications [18]. Moreover, a decrease of the protective effectiveness afforded by BTA treatment applied on copper artefacts exposed over long periods in an uncontrolled museum atmosphere was sometimes noticed [19]. On the other hand, BTA is considered toxic for many plants, aquatic organisms and bacteria [20].

Several attempts have been made in the last years for finding new corrosion inhibitors that might replace BTA. The anticorrosive properties of various triazole [21], imidazole [22] and thiadiazole [22–24] derivatives applied on bronze specimens covered with artificial or natural patina were investigated; some were proven to be promising candidates for the protection of bronze artefacts covered with patina layers. For example, tests carried out in simulated polluted acidic rain of pH 3 showed that certain thiadiazole derivatives allow the stabilization of the artificial patina, leading to the protection of bronze substrate [23]. It was also demonstrated that their effectiveness significantly increases with the immersion time, while BTA progressively loses its protection ability in the same conditions.

New protective coatings for use on chemically and electrochemically formed patinas on recent bronze were obtained by addition of different organic inhibitors in ethylmetacrylate/methyl metacrylate copolymer (Paraloid B44) [15,25] Although a significant corrosion protection was achieved, when inhibitors like BTA or 1-(*p*-tolyl)4-methyl imidazole (TMI) were applied by brushing contact over the patina layers in an ethyl-acetate solution of Paraloid B44, their protectiveness decreases over the exposure time to a simulated urban rain (pH 5). Moreover, the Paraloid layers containing inhibitors were found to be only slightly effective on electrochemically patinated bronzes, and had almost no effect on chemically patinated surfaces.

Based on our previous experience on bronze corrosion inhibition [23,24] and taking into consideration that the thiadiazole derivatives, *i.e.* 2-mercapto-5-amino-1,3,4-thiadiazole (MAT) and 2-mercapto-5-methyl-1,3,4-thiadiazole (MMeT) were found to be promising candidates for BTA replacement [23], in the present paper, new coatings based on a nitrocellulose lacquer incorporating MAT and MMeT for the protection of artificially patinated bronzes exposed indoors were developed. For comparison, the inhibiting effect of the nitrocellulose lacquer coating containing BTA was also examined. The nitrocellulose lacquer is currently used in the conservation practice for the stabilization of iron and bronze archaeological artefacts exposed indoor [26]; however, uncontrolled museums atmosphere might lead to its deterioration during time. This is why, in order to test the anticorrosive properties of the nitrocellulose lacquer coatings incorporating organic inhibitors and to be sure that they are long-term resistant indoor, more aggressive conditions simulating an urban rain in outdoor exposure, were chosen.

The studies were performed mainly by electrochemical impedance spectroscopy, because the technique allows the time monitoring of the corrosion parameters corresponding to patinated bronzes covered with nitrocellulose lacquer containing various organic inhibitors.

The protective performances of the coating were explored for approximately three months of exposure to intermittent immersion in an acidic carbonate/sulphate solution of pH 5 aiming to simulate the wet and dry cycles existing in the environment. Optical microscopy examination of patinated bronze surface covered with blank and inhibitors-containing nitrocellulose lacquer was used to determine the thickness of the coatings. In addition, Fourier transformed infrared spectroscopy (FT-IR) was employed to study the reactions between the organic inhibitors and nitrocellulose lacquer functional groups.

2. Experimental

2.1. Materials

Rectangular-shaped bronze sheets (10 mm × 10 mm of exposed area) were used as working electrodes. Chemical composition of the bronze (wt.%) was as follows: Cu-93.66, Sn-6.10, Zn-0.1, Fe-0.02, Pb-0.01, and P-0.11. After being provided with an electrical contact on the backside, the bronze sheets were covered with a cataphoretic paint (PGG W975 + G323) to avoid the electrolyte infiltration. The bronze sheets, now prepared, were embedded into epoxy resin (Bueler – Epoxycure®) and polished using successive grades of silicon carbide paper up to 2400 grit, in order to obtain a smooth and planar surface. Finally, the samples were rinsed thoroughly with distilled water and ethanol. The counter and reference electrodes were a large platinum grid and calomel in saturated KCl (SCE), respectively.

2.2. Artificial patina formation

The artificial patina was simultaneously synthetized on six bronze electrodes, which were connected in parallel into an electrochemical cell under potential regulation, according to a procedure previously described [22]. The electrolyte used for the artificial patina preparation was an aqueous and aerated solution of 0.2 g/L $NaHCO_3$ + 0.2 g/L Na_2SO_4 at pH 8.5. As mentioned before [27], this solution is expected to produce a patina characteristic of an urban environment, since SO_4^{2-} ions are one of the main pollutants in metropolitan atmosphere due to the industrial activity and cars emissions.

The EDX analyses of the pale blue to green patina layer formed on the bronze electrodes showed that it contains Cu(OH), SnO_2 or $Sn(OH)_4$, sulphate and carbonate ions [22]. The green patina is a good representative of the Type I corrosion structure found on ancient bronzes [3].

2.3. Coatings

A commercial nitrocellulose lacquer (Vestel, Romania) was studied as coating of patinated bronze specimens. Three organic compounds that have been previously reported as efficient corrosion inhibitors of the naked [23,24] and artificially patinated bronze samples [22,23] were added into the nitrocellulose lacquer coating. The investigated organic compounds were: 2-mercapto-5-amino-1,3,4 thiadiazole (MAT), 2-mercapto-5-methyl-1,3,4-thiadiazole (MMeT) and benzotriazole (BTA); their molecular structure is presented in Scheme 1.

In order to prepare the coatings with inhibitors, appropriate amounts of the above-mentioned organic compounds were weighted and added into the nitrocellulose lacquer, in order to obtain the following concentrations: 5 mM for MAT and MMeT and 1 mM for BTA. The concentrations of the inhibitors in the nitrocellulose lacquer were selected due to the results of our former studies