THE TESTING OF NATURAL CORROSION INHIBITORS CYSTEINE AND MATURE TOBACCO FOR TREATING MARINE COMPOSITE OBJECTS IN PEG400 SOLUTIONS

Angeliki ZACHAROPOULOU[1*], Georgios BATIS[1],
Vasiliki ARGYROPOULOU[2], Elodie GUILMINOT[3]

[1] Department of Materials Science and Engineering, School of Chemical Engineering, National Technical University of Athens, 9 Heroon Polytechniou Str., 11580 Zografou Athens, Greece
[2] Department of Conservation of Antiquities & Works of Art, Technological Educational Institution of Athens, Ag. Spyridonos, Aigaleo, Greece
[3] Arc'Antique Laboratory, GPLA, 26 rue de la Haute Forêt, 44300 Nantes, France

Abstract

The paper presents the testing of two nontoxic corrosion inhibitors for treatments of marine metal composite artefacts in Polyethylene Glycol (PEG) 400 solutions. The effectiveness of L-cysteine and mature tobacco to slow down the corrosion of copper and iron alloys during PEG400 treatments was investigated using electrochemical techniques. Potentiodynamic polarization measurements were carried out on polished wrought iron and brass metal samples taken from the 1868 shipwreck 'Patris' in 20% (v/v) PEG400 in deionized water with and without each corrosion inhibitor. L-Cysteine was found at a concentration of 1% (w/v) to act as a cathodic corrosion inhibitor for brass in 20% (v/v) PEG400 solutions, passivating the metal between -0.4V and -0.2V vs. SSE. Mature tobacco was found not to act as corrosion inhibitor for wrought iron at 1% (w/v) in 20% (v/v) PEG400 solutions, and more research is needed to find a derivative of this type of corrosion inhibitor to improve its corrosion inhibition efficiency at near-neutral pHs.

Keywords: *Nontoxic corrosion inhibitor; L-Cysteine; Mature tobacco; PEG400; Metal composite artifacts.*

Introduction

Conservation treatments for marine composite artefacts are often the most difficult to stabilize and treat, especially when an object is made up of different types materials that cannot be separated, such as organic materials (wood, textile, or leather) with either iron or copper alloyed components. For waterlogged organic materials usually polyethylene glycol (PEG) or other bulking solutions are used to remove the water and consolidate the material. These treatments are carried out at pH 4.5-8.5 and cause the corrosion of iron and copper metal or the dissolution of the corrosion products in the patina. This will result not only in a loss of metal during treatments, but also the organic material will become additionally stained with metal corrosion products. A corrosion inhibitor is required during PEG treatments to minimize the

---

* Corresponding author: aggeliki.zaxaropoulou@gmail.com

corrosion of the metal during the process or the dissolution of metal oxides. While past research has focused on the inhibition properties of Hostacor®IT, phosphates, benzotriazole, and even PEG itself on wet composite artefacts containing iron or copper alloys [1-2] the effectiveness of these corrosion inhibitors in real situations varies depending on many factors [3-5]. The duration of storage of treatment solutions, the presence of certain ions (chloride, metal etc.) at the corrosion/metal interface, as well as the types of corrosion products can result in these corrosion inhibitors as being ineffective. For example, Hostacor®IT was found to act as an anodic corrosion inhibitor in PEG400 solutions, where it is adsorbed onto the anodic areas of the metal and cause a positive shift in the corrosion potential of the metal. However, when chlorides are present at the iron anodic sites, a competitive adsorption between the chlorides and anodic inhibitor takes place making the corrosion inhibitor ineffective. For copper alloys containing chlorides, the corrosion inhibitor benzotriazole is commonly used to stabilize artifacts with bronze disease. Given the toxicity of benzotriazole, research in conservation has focused on finding a suitable replacement, such as L-cysteine [6]. Despite the vast number of corrosion inhibition investigations in conservation, there are still few studies directed towards the application of non-toxic organic compounds, especially amino acids (L-cysteine) for copper alloys [7–9] and plants (mature tobacco) for iron alloys [10-12]. Tobacco and its extracts as well as L-cysteine have been tested and found by industry to be effective as a corrosion inhibitor for various metals in different media [10]. Furthermore, L-cysteine has been found by industry to inhibit enzymatic browning [13] or for its antibacterial properties [14] on various organic materials. This paper presents the research carried out on the application of mature tobacco and L-cysteine as a corrosion inhibitor for iron and copper alloys respectively in deionized water and PEG400 solutions.

Materials and Methods

L-Cysteine

L-Cysteine (purity 99^+ %) was tested as corrosion inhibitor of copper alloys (Fig. 1). L-cysteine is a non-toxic amino acid that is completely soluble in aqueous media and produced with high purity at low cost. These properties justify its use as a corrosion inhibitor [15]. For the experiments, fresh solutions of L-cysteine and PEG400 were made up each day, and during the day stored in a fridge.

Mature Tobacco

Mature tobacco is a plant within the genus *Nicotiana* of the *Solanaceae* (nightshade) family (Fig. 2). While there are more than 70 species of tobacco, the chief commercial crop is *N. tabacum*. Tobacco plants contain approximately 4,000 chemical compounds – including terpenes, alcohols, polyphenols, carboxylic acids, nitrogen – containing compounds (nicotine), and alkaloids.

Fig. 1 L- Cysteine

Fig. 2 Mature Tobacco

These may exhibit electrochemical activity such as corrosion inhibition [10]. For this study, mature (10 years old) tobacco coming from the region of Agrinio (Greece) was used. It was prepared by taking the dried leaves of the mature tobacco and grinding them into a powder using a mortar and pestle. The powder was then made up as a 1% (w/v) solution in deionized water, which was shaken mechanically for an hour and filtered using filter paper. For the experiments, fresh solutions for mature tobacco with PEG400 were made up each day and kept in the fridge during the day.

The iron and brass samples used for the experiments were taken from a wrought iron rod (1.0m length) with brass knobs at both ends found on the 1868 Shipwreck 'Patris'. Figure 3 and 4 provide images of the microstructure of each metal obtained by a NIKON Epiphot 200/300 Inverted Metallographic microscope. Figure 3 indicates that the metal is wrought iron made by the process of puddling based on the shape of slag inclusions. In Figure 4, the brass is a sand cast alloy, and the chemical analysis using SEM-EDAX (type GEAN GSM 6510) with low vacuum and X-ART detector (working distance: 20mm) found its composition in weight % as 57 Cu, 34 Zn, 2.5 Sn, 2.0 Pb, and the rest as contaminants such as oxygen and iron. From each metal, two polished working electrodes (diameter: 1.0cm and thickness: 3.0mm) were prepared for the rotating disc electrode so as to allow for more repetitive measurements.
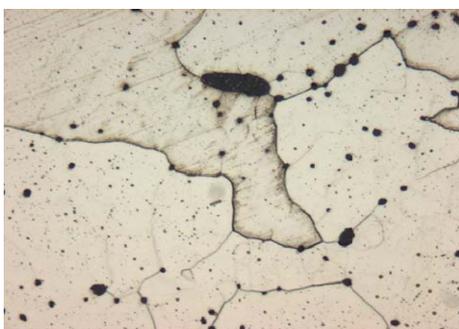

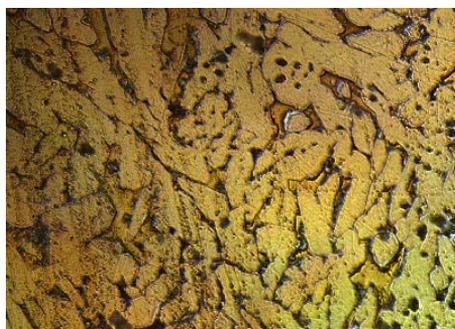**Fig. 3.** Microstructure of wrought iron sample (X200)

Fig. 4. Microstructure of brass alloy sample (X200)

Potentiodynamic experiments were carried out at Arc'Antique, France using a Faraday cell with a rotating disk electrode as the working electrode (i.e., wrought iron or brass alloy), with and without 1% (w/v) mature tobacco and 1% (w/v) cysteine respectively in 20%(v/v) PEG400 solutions in deionized water. Experiments were controlled at a constant temperature 30 ± 1ºC, in naturally aerated solutions. The experimental setup for conducting electrochemical measurements included a BioLogic SAS-SP 150 potentiostat connected to a computer to record the experimental data. Cathodic and anodic polarization curves were repeated three times for each experiment with and without inhibitor to check the results using interchangeably one of the two working electrodes for each metal. Each rotating disk electrode as the working electrode (i.e., wrought iron or brass alloy) was then polished with a series of silicon carbide papers up to 4000 grit. After which, it was rinsed with pure ethyl alcohol in an ultrasonic bath, and dried with a hair dryer. For each experiment, the working electrode was polished again to ensure reproducibility of the results. The procedure was as follows:

Begin by measuring the Open Circuit Potential (OCP) for 30 minutes.

After measuring OCP, select either +50mV as the starting potential for anodic polarization or -50mV for cathodic polarization.

Scan rate of the potential for each experiment was 1 mV/sec.

Cathodic polarization for L-cysteine experiments using brass with a potential limit of -1.5 V vs. SSE was selected.

Cathodic polarization for mature tobacco using iron with a potential limit of -2V vs. SSE was selected.

During anodic polarization, a final potential of +1.2 V vs. SSE was selected for both metals. Figure 5 gives a schematic diagram of the Faraday cell used for the experiment.
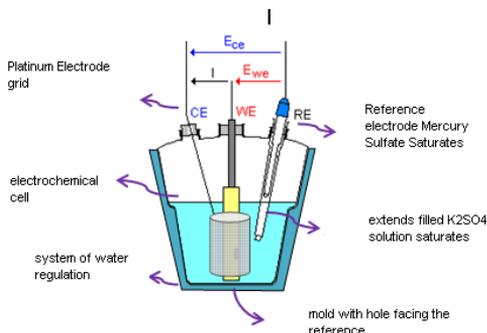

Fig. 5. Faraday cell used in the experiment

Results and Discussions

The results for anodic polarization show that the presence of L-cysteine decreases the corrosion rate (i.e. i_{corr} decreases) and forms a passive film for the brass sample until -0.2V vs SSE (see Fig. 6). However, for mature tobacco the corrosion rate increases (i.e. i_{corr} increases) for the wrought iron sample in 20% (v/v) PEG400 solutions when compared to the same experiment without inhibitor (see Fig. 7).

Also, the open circuit potential or E_{corr} prior to each experiment with cysteine shifts to more negative values than without. The anodic and cathodic polarization experiments were repeated three times with and without 1 % (w/v) cysteine in 20% (v/v) PEG400 solutions and produced similar shaped curves, but were not reproducible. It was found that the OCP varies depending on which of two brass samples (electrodes) were used, indicating that after repeated polishing of the sample, the surface area was not exactly identical for both working electrodes of the brass samples during the experiments. However, the results clearly indicate that cysteine is acting in the PEG400 solutions as a cathodic inhibitor in near-neutral pHs.
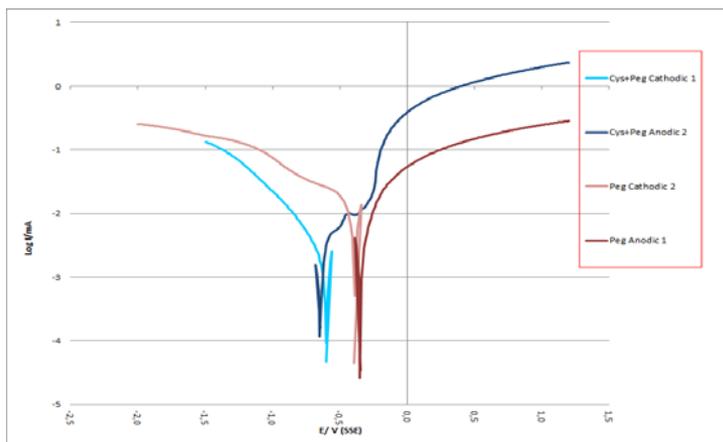

Fig. 6. Polished Brass in 20% (v/v) PEG400 in deionized water with and without cysteine (1%w/v)
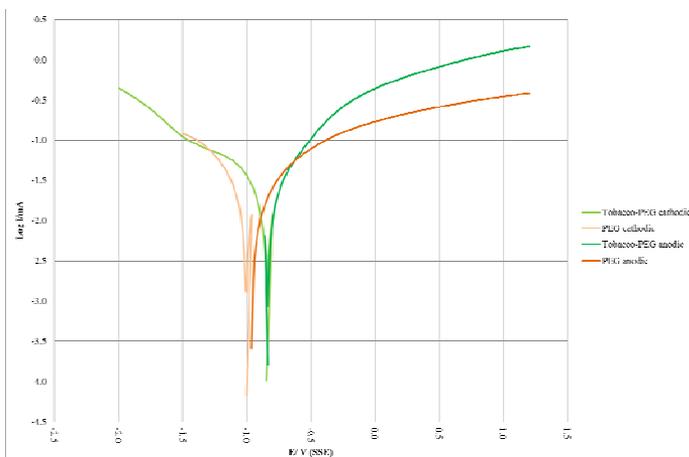
Fig. 7. Polished wrought iron in 20% v/v PEG400 in deionized water with and without mature tobacco (1% w/v)

The transfer of oxygen from the bulk solution to the copper/solution interface plays a critical role at the rate of oxygen reduction. The adsorbed layer of cysteine or its complex behaves as a cathodic inhibitor to Cu corrosion by retarding the transfer of O_2 to the cathodic sites of the Cu surface [16, 17].

For mature tobacco, the OCP values shift to more positive values than without inhibitor. However, this shift is not significant, and the curves for each anodic and cathodic polarization experiments are reproducible and similar (Fig. 7).

Conclusions

L-cysteine was found to inhibit corrosion of copper alloys in PEG400 solutions, and acts as a cathodic inhibitor. Research is now underway to test the effect of the inhibitor on copper alloys with corrosion products, since preserving the patina of the metal also plays an important role in conservation. The varying effects of L-cysteine on different types of corrosion products at near-neutral pH have been previously investigated and largely depends on their crystallinity and the types of metal ions that can catalyze the oxidation of L-cysteine to cysteine [18]. The results for mature tobacco were disappointing, and indicate that a further research is needed in preparing possibly a derivative of the mature tobacco solutions to help increase the corrosion inhibition efficiency for iron alloys in near-neutral solutions.

Acknowledgements

References

[1] V. Argyropoulos, J.J. Rameau, F. Dalard, C. Degrigny, *Testing Hostacor IT as a corrosion inhibitor for iron in polyethylene glycol solutions,* **Studies in Conservation**, **44**(1), 1999, pp. 49–57.

[2] E. Guilminot, F. Dalard, C. Degrigny, *Mechanism of iron corrosion in water-polyethylene glycol (PEG400) mixtures*, **Corrosion Science, 44**, 2002, pp. 2199-2208.

[3] A.V. Sandu, A. Ciomaga, G. Nemtoi, M.M.A. Abdullah, I. Sandu, *Corrosion of Mild Steel by Urban River Water,* **Instrumentation Science and Technology, 43**(5), 2015, pp. 545-557.

[4] A.V. Sandu, C. Bejinariu, G. Nemtoi, I.G. Sandu, P. Vizureanu, I. Ionita, C. Baciu, *New Anticorrosion Layers Obtained by Chemical Phosphatation,* **Revista de Chimie, 64**(8), 2013, pp. 825-827.

[5] A.V. Sandu, C. Coddet, C. Bejinariu, *A Comparative Study on Surface Structure of Thin Zinc Phosphates Layers Obtained Using Different Deposition Procedures on Steel,* **Revista de Chimie, 63**(4), 2012, pp. 401-406.

[6] M. Gravgaarda, J. van Lanschot, *Cysteine as a non-toxic corrosion inhibitor for copper alloys in conservation,* **Journal of the Institute of Conservation, 35**(1), 2012, pp. 14-24.

[7] G. Moretti, F. Guidi, *Tryptophan as copper corrosion inhibitor in 0.5 M aerated sulfuric acid,* **Corrosion Science, 44**, 2002, pp. 1995-2011.

[8] G.K. Gomma, M.H. Wahdan, *Effect of temperature on the acidic dissolution of copper in the presence of amino acids*, **Materials Chemistry and Physics, 39**, 1994, pp. 142-148.

[9] D.Q. Zhang, L.X. Gao, G.D. Zhou, *Inhibition of copper corrosion in aerated hydrochloric acid solution by amino-acid compounds*, **Journal of Applied Electrochemistry, 35**, 2005, pp. 1081-1085

[10] C.A. Loto, R.T. Loto and A.P.I. Popoola, *Synergistic Effect of Tobacco and Kola Tree Extracts on the Corrosion Inhibition of Mild Steel in Acid Chloride*, **International Journal of Electrochemical Science, 6**, 2011, pp. 3830 – 3843

[11] C.A. Loto, R.T. Loto and A.P.I. Popoola, E*lectrode Potential Monitoring of Effect of Plants Extracts Addition on the Electrochemical Corrosion Behaviour of Mild Steel Reinforcement in Concrete*, **International Journal of Electrochemical Science, 6**, 2011, pp. 3452 - 3465

[12] G.D. Davis, J. A. von Fraunhofer, L.A. Krebs, C.M. Dacres, *The Use of Tobacco Extracts as Corrosion Inhibitors*, **Corrosion 2001,** Paper 1558 (NACE, Houston, TX, March 2001).

[13] T. Rithmanee, P. Intipunya, *Effects of High Power Ultrasonic Pretreatment on Physicochemical Quality and Enzymatic Activities of* Dried Longan, **Journal of Agricultural Science, 4**(11), 2012, pp. 299-306.

[14] E. Caldeira, E. Piskin, L. Granadeiro, F. Silva, I.C. Gouveia, *Biofunctionalization of cellulosic fibres with l-cysteine: Assessment of antibacterial properties and mechanism of action against Staphylococcus aureus and Klebsiella pneumoniae,* **Journal of Biotechnology, 168**, 2013, pp. 426-435.

[15] A.B. Silva, S.M.L. Agostinho, O.E. Barcia, G.G.O. Cordeiro, E. D'Elia, *The effect of cysteine on the corrosion of 304L stainless steel in sulphuric acid*, **Corrosion Science, 48**, 2006, pp. 3668–3674

[16] K.M Ismail, *Evaluation of cysteine as environmentally friendly corrosion inhibitor for copper in neutral and acidic chloride solutions,* **Electrochimica Acta, 52**, 2007, pp. 7811-7819.

[17] E. Guilminot, J-J. Rameau, F. Dalard, C. Degrigny, X. Hiron, *Benzotriazole as inhibitor for copper with and without corrosion products in aqueous polyethylene glycol,* **Journal of Applied Electrochemistry, 30**(1), 2000, pp. 21-28.

[18] R.M. Cornell, I.R. Giovanoli, W. Schneider, *Effect of Cysteine and Manganese on the crystallization of noncrystalline iron(III)hydroxide at pH 8*, **Clays and Clay Materials, 38**(1), 1990, pp. 21-28.