NORTH DAKOTA STATE UNIVERSITY
FINAL REPORT
TO THE
NATIONAL CENTER FOR PRESERVATION TECHNOLOGY AND TRAINING
2000 GRANT PROGRAM

1. Project type: Environmental Effects of Outdoor Pollutants on Cultural Resources

2. Project title: Development and Testing of Organic Coatings for the Protectio of Outdoor Bronze Sculpture from Air-Pollutant Enhanced Corrosion – Year 2

3. Recipient: North Dakota State University
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Table of Contents

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Grant Number: MT-2210-0-NC-20

Executive Summary

The second year of research focused on exploration of new coating technologies that would be appropriate for outdoor bronze sculpture. The coatings currently under investigation are a fluorocopolymer blended with various acrylics, conductive polymers, BTA pretreatments, and a very fine titanium dioxide. These coatings are being studied on both rolled bronze and on satin-finish, cast monumental bronze substrates by the use of electrochemical impedance spectroscopy (EIS). In addition, an international survey focusing on the techniques used by conservators for metal preservation is underway. With this information we hope to better understand the problems, practices, and ethics surrounding the conservation of bronze sculpture. In addition we hope to be able to focus our research to techniques and materials that would be acceptable and potentially adoptable by the conservation community.

Introduction

This research addresses the need for development of an improved protective coating for outdoor bronze. Atmospheric corrosion is becoming more prevalent throughout the world and the result is an increasing production of corrodants such as SO_x, NO_x, CO_2, and chlorides. These corrodants affect various materials including bronze. Unprotected outdoor bronze corrodes readily when an electrolyte comes in contact with the metal. The metal, acting as the anode, readily oxidizes while a cathodic reduction reaction of O_2 and H_2O occurs. Multiple parameters that affect the severity of atmospheric corrosion include: temperature, corrosion products, passive film formation, electrolyte thickness, and metal composition.[1] The location of bronze sculpture in high pollution urban areas is potentially very harmful, reduces their longevity, and changes their original appearance.

Protection from bronze corrosion is thus very important when trying to conserve the bronze sculpture situated in such a chemically hostile environment. Corrosion of the bronze leads to not only discoloration of the original surface but also leads to pitting of the bronze surface. Pitting occurs when soluble corrosion products are formed. During rain or other forms of precipitation, the corrosion products are easily washed away and leave behind a pit within the bronze. Both pitting and the discoloration lead to a loss in aesthetic quality of the monument. A conservator attempts to maintain the original intent of the artist by protecting with the least intrusive means possible. The ideal coating would thus be clear, removable, and protect the bronze by preventing the corrosion from occurring.

Minimizing the corrosion of bronze can be done by using coatings on the monuments. Coatings provide a barrier between the corrodants and the metal substrate. By various mechanisms the coating system inhibits corrosion. Currently throughout the United States the common coating system used to protect bronze from corrosion is an Incralac® + wax system.[2] Incralac® is an acrylic based polymer that is soluble in toluene, while the wax is also considered removable. Incralac® + wax has proven to be a better coating system compared to wax by itself under normal weathering of. Incralac® has proven to have limitations. Incralac® is difficult to apply, requires toxic solvents to remove, and its lifetime ranges from 3-5 years.[3] Thus every 3-5 years, efforts must be made to remove the old coating system and then reapply a new coating. Minimizing this step of removing and then reapplying a new coating can be achieved by finding a longer-lived coating system to replace the Incralac® + wax system. Such a new coating that would have a longer lifetime would require less time, money, and energy spent on conservation efforts. Minimizing the number of conservation treatments would ultimately minimize potential harm to the bronze during the coating removal and reapplication steps.

Methods and Materials

Bronze samples were cast at the Johnson Atelier in Mercerville, NJ. The bronze was cast using Leaded Red Brass ingots (ASTM B30) purchased from the Colonial Metals, Company. The composition of the bronze is 85% copper, 5% tin, 5% zinc, and 5% lead. One hundred 4' x 6' samples were sand cast, at approximately a ¼' thickness. After casting, a portion of these bronze plates were polished to a satin finish. This finishing procedure consisted of sanding with an 80-grit disc, 120-grit disk, and a 4.5" 3M blue surface conditioning pads. This was followed by a step using an orbital sander with 220 grit abrasives, and finally a red 3M conditioning pad. One third of the 100 panels cast are being treated with a French brown patina. The process used to patinate these is as follows: First, the samples are sanded using a 120 grit disc, then are glass bead blasted. Liver of Sulfur (ammonium sulfide) is then applied cold. The surface then is rubbed with a red 3M pad and rinsed with distilled water. The sample is then heated with a propane torch, and a ferric nitrate/ distilled water solution is applied.

The bronze samples have been examined using X-ray Fluorescence (XRF) and Scanning Electron Microscopy (SEM). It was found from both, that the composition of the bronze varies slightly across the surface, but the general composition of the alloy is indeed 85% Cu, 5% Sn, 5% Pb, 5% Zn. It was determined from XRF that Cu-Sn-Zn compounds exist, but the lead has remained in its elemental form.

In addition, to the cast bronze, rolled bronze is being used for the initial studies. The rolled bronze is Lullaby 425 spring loaded, purchased from Guardian Metal Sales, Inc. and is composed of the following composition; 87.547% copper, 0.005 % lead, 0.038% iron, 10.600% zinc, 1.760% tin.

Electrochemical methods such as EIS are techniques that provide a quantitative analysis of a corroding material.[4] The impedance of protective coatings is determined by application of a small, sinusoidal current (1-10 mV generally) to an electrochemical cell in which the coated panel is the working electrode, with an SCE and a platinum mesh working electrode.

EIS is an electrochemical method that can be utilized to characterize the corrosion protection of coatings.[5,6,7,8,9,10] As the corrosion protection of the coating decreases so does its impedance value. An increased amount of electrolyte penetrating into the coating is indicative of poor corrosion protection and increases the capacitance of the system.[9] The capacitance increase shows its effects in the higher frequency portions of the EIS spectrum, but at low frequencies is identified with an increase in water uptake in the film and a decrease in film resistance.

EIS analysis of the protective coatings on monumental bronze was determined by application of an alternating current of 5mV to the cell. The electrochemical cell consisted of a saturated calomel reference electrode and a platinum mesh counter electrode that were immersed in dilute Harrison electrolyte solution. The electrolyte stayed in contact with the working electrode sample by using an o-ring clamp with an area of 7.0 cm^2. A Gamry PC3 potentiostat with CMS 100 software was used to collect the data over the frequency range of 5000 to 0.1 Hz. The schematic of the electrochemical set-up is shown in Figure 9.

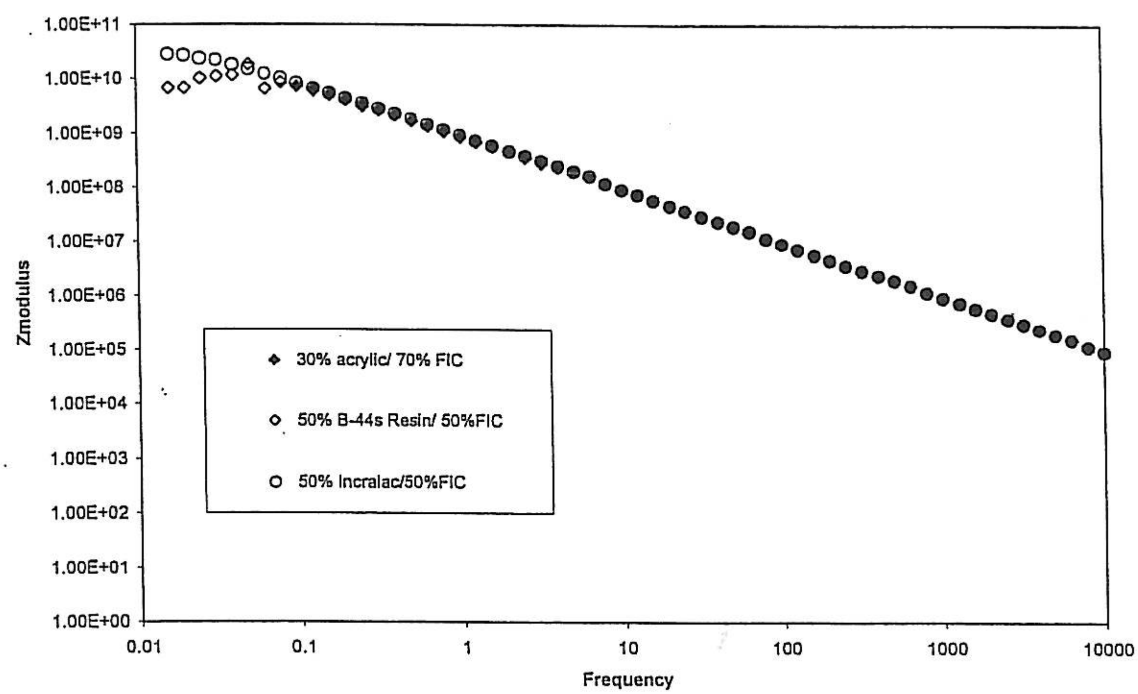
Fluoropolymer Study

In a search for a coating that would be suitable for an outdoor bronze, initial investigation of a fluoropolymer based on polyvinylidene fluoride (PVDF) shows promising results. Fluoropolymers are known for their exterior durability, chemical resistance and good flexibility, all important features for an outdoor coating. Initial studies also indicate that the fluoropolymer is removable with a polar solvent, such as acetone and is also optically transparent in the visible region of the spectrum.

The PVDF that is being explored is Kynar® RC-10,052 PWD PVDF, supplied by Autofina. The PVDF is a hexafluoropropylene- vinylidine fluoride copolymer. It was found that this copolymer can be dissolved in acetone, and forms a viscous, but workable material at 8.0 wt.% PVDF. Unfortunately this material yields a film with very poor adhesion to the bronze substrate. The chemical inertness of PVDF also makes it difficult to increase its adhesion by itself.[11] To increase adhesion of the PVDF, we have blended the copolymer with an acrylic copolymer. The acrylic used was Paraloid B-44, which is an acrylic copolymer resin made by Rohm and Haas. This acrylic also happens to be the base for Incralac, currently the most popular coating used by conservators on bronze sculpture. An acrylic copolymer was chosen to blend with the copolymers, because of its known properties of clarity and the ability to removability . The PVDF/acrylic blend has increased film adhesion to an "average" range. We are currently studying the fluorpolymer blended with another Rhom and Hass acrylic, Paraloid A-21, in hopes of furthering the adhesion of theresultant fluorocarbon-based film

Initial electrochemical studies indicate that the fluorocarbon-acrylic blend has the potential of being an excellent coating. The following figure demonstrates the initial electrochemical impedance spectroscopy (EIS) results of the blend on rolled bronze.

Figure 1. EIS Bode Plots of Fluorocarbon/ Acrylic Blends



The low frequency points of the Bode plot, indicate that the PVDF/acrylic blend is a very high resistance coating. Further studies will again focus on attempts to increase the adhesion of the coating, along with artificial weathering of the coating on cast bronze.

Conductive Polymers

Conductive polymers have been the subject of studies looking for new pretreatments for metal substrates. The conductive polymers have been shown to provide excellent protection for metals. Because of their conductive properties, most of the polymers are not clear. There are a very few references to optically clear conductive polymers.[12,13,14,15] The references indicated that the optically clear conductive materials are difficult to work with and are often not transparent. Nerveless, because of the protective properties of the conductive polymers on aluminum, the conductive polymer, poly(3-octylpyrrole) (POP) was studied on cast bronze. The POP with two different dopants was studied. The first has the dopant,was p-toluenesulfonate (pTS) and the second dopant was a mixture of pTS and sodium perchlorate (ClO_4). The conductive polymers were dissolved as a 50/50 weight % solution in carbon tetrachloride and dichloromethane, and then were cast onto the bronze. The POP coatings formed a dark, patina-like film over the bronze. The impedance of the coatings were then monitored by EIS. The durability of the coating was then evaluated by immersing the sample in dilute Harrison's solution over the course of 29 days. In addition, bare bronze was also tested by immersion in dilute Harrison's solution for 65 days. The Bode plots of the data measured from these samples can be viewed in Figures 2-4.

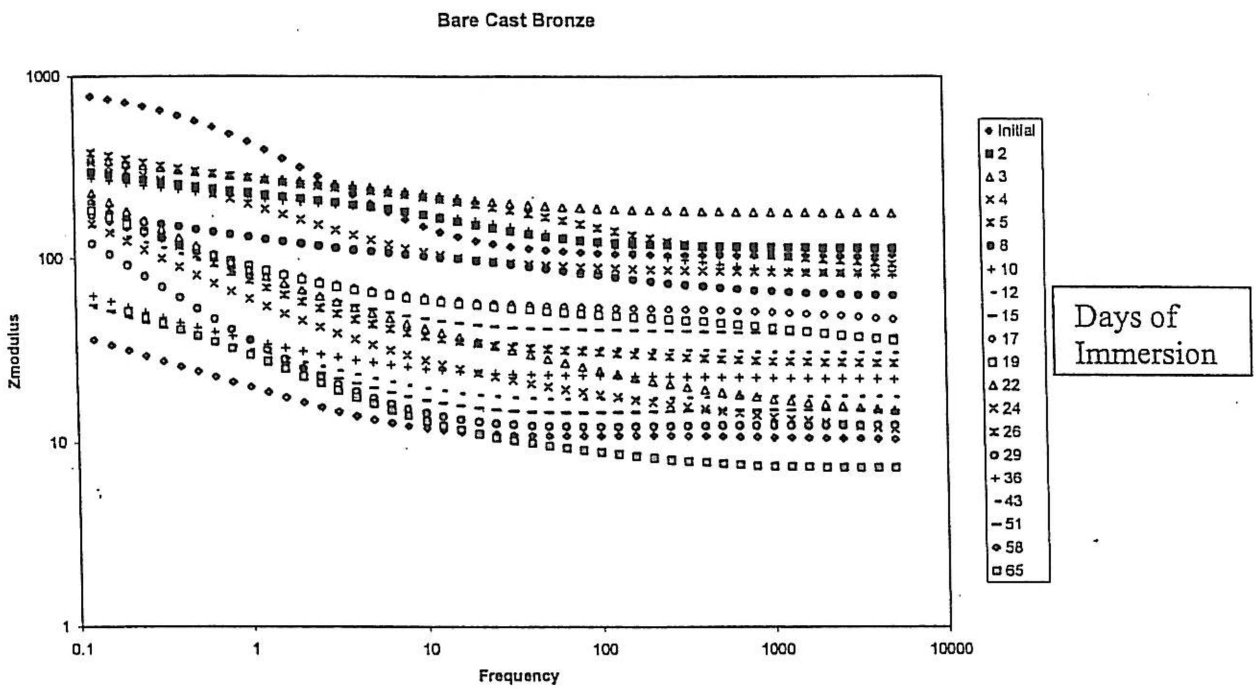


Figure 2. Bare Cast Bronzed in Immersion

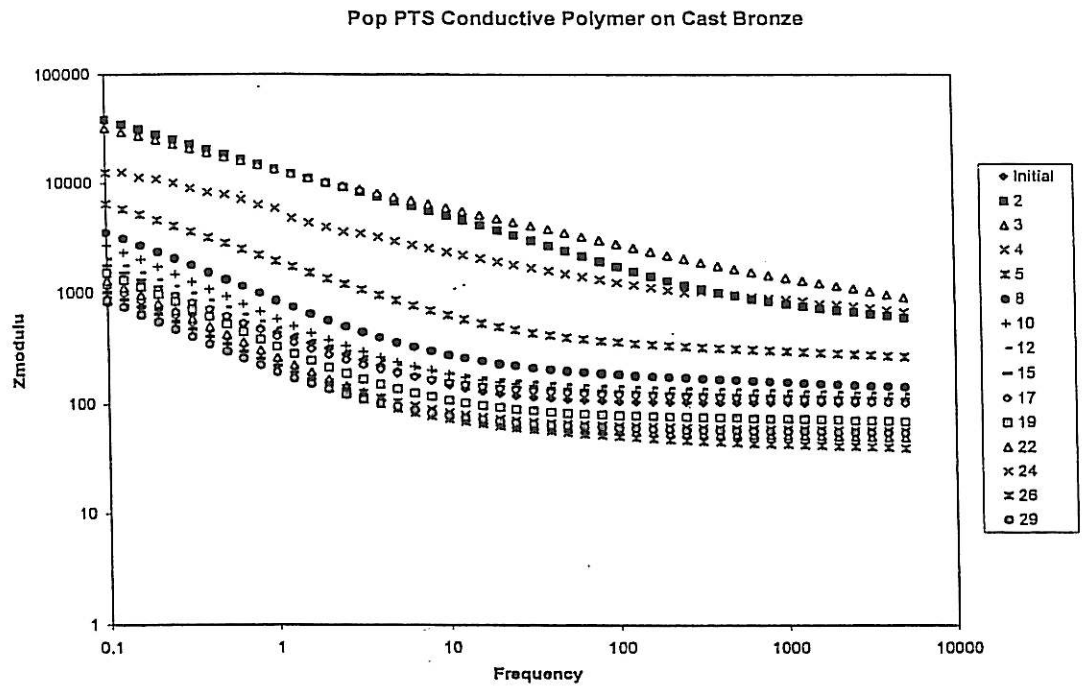


Figure 3. POB doped with PTSA in Immersion.

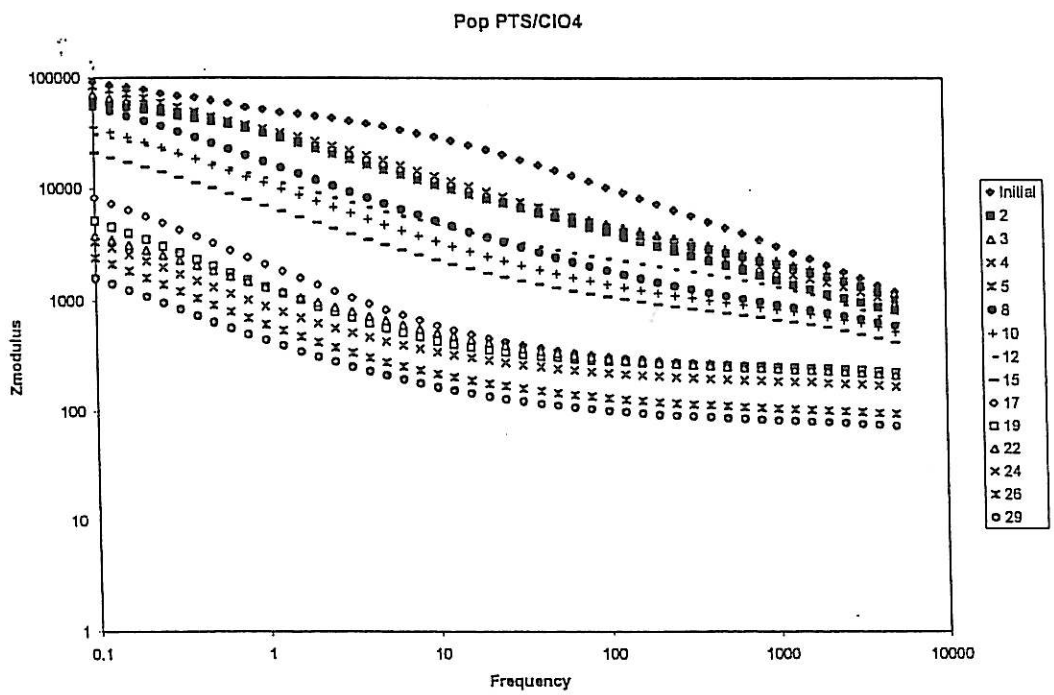


Figure 4 doped with PTSA/CLO$^{-}_{4}$ in Immersion.

The two conductive polymers provided protection for the bronze for 29 days, after which time the impedance fell to the levels of the bare bronze. These results indicate that conductive polymers could be used on bronze as a very effective pretreatment, if optical clarity is not a requirement. If absolute replication of appearance is needed, conductive polymers could be used with patinated materials, and would provide corrosion protection to this substrate without interfering with its appearance

BTA Pretreatments

Benzotriazole (BTA) films were again tested for their protection of rolled bronze. The bronze samples were immersed in various BTA solutions for 1, 10, 100, or 1,000 minutes. Each sample was then tested using electrochemical impedance spectroscopy (EIS). Overall results show that BTA provides only minimum protection against immersion in an acid rain solution, but under specific preparations does afford significant initial resistance.

BTA has been used for years to stabilize objects that are housed inside, but BTA is also being applied on outdoor sculptures. Although there have been many empirical studies on the effect of BTA on bronze sculpture there has not been a study measuring the corrosion protection of the film in an outdoor environment.[16,17] Hence a standard method of treatment used in the field of Objects Conservation does not exist.

The rolled bronze samples were prepared in several steps. First the bronze plates were sanded using 2400, 3600, 4000, 8000, and 12,000 grade micromesh to remove any oxidation layer or impurities that might be on the sample. The samples were degreased with hexane and immersed in a solution of 1.5%, 3%, 5%, or 10.5% BTA in ethanol for 1, 10, 100, or 1000 minutes. A variety of different solvents were used to try to dissolve the BTA, including water, acetone, ethanol and isopropanol. It was found that ethanol best solvated the BTA. The highest concentration of BTA in ethanol that would stay in solution was10.5%.

The samples were monitored using Electrochemical Impedance Spectroscopy (EIS) during immersion. An application of an alternating current of 5mV was applied to the electrochemical cell. The cell consisted of a saturated calomel reference electrode and a platinum mesh counter electrode that was immersed in dilute Harrison electrolyte solution. A 7.0 cm2 area of the working electrode was exposed to the electrolyte. A Gamry PC4 potentiostat with CMS 100 software was used to collect the data over the frequency range of 5000 to 0.1 Hz.

The following figure illustrates the low frequency impedance values initially and after 24 hours of immersion in the dilute Harrison's solution.

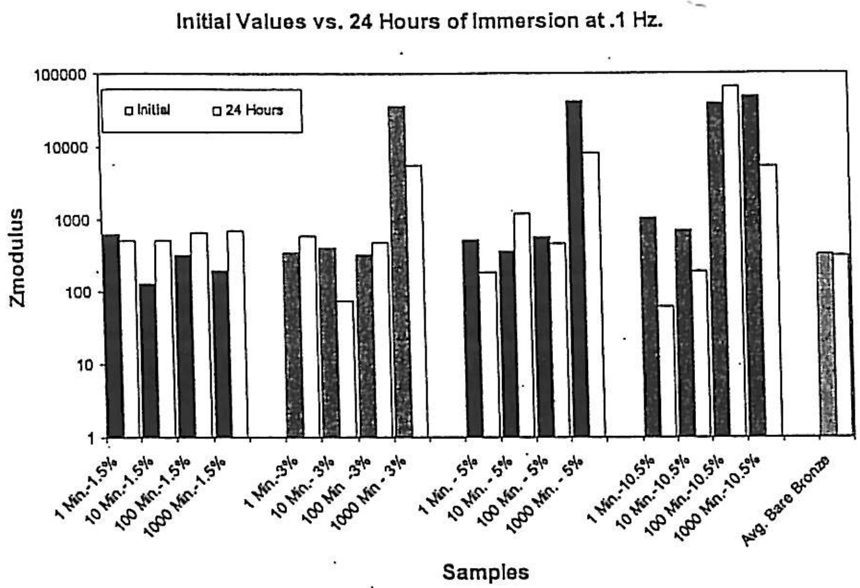


Table 5. Low Frequenqy |Z| values for Samples Dipped in BTA Solutions

The EIS results indicate that the longer immersion times of samples provide more protection to the coating. Because large monuments can not be immersed in solutions, this study indicated that at low immersion times (or brushing contact) any concentration of the BTA solution will provide limited, but equal protection. It is possible that the BTA does little to protect the bronze from corrosion, but helps more in the absorption of ultra violet light. The 10.5% solution of BTA in ethanol is the most promising, as seen in the above plot. This concentration also left discoloration and crystalline patches on the surface of the bronze, after immersion, and therefore can not be recommended for use.

The figure below is a Bode plot of the initial BTA values, including the bare bronze.

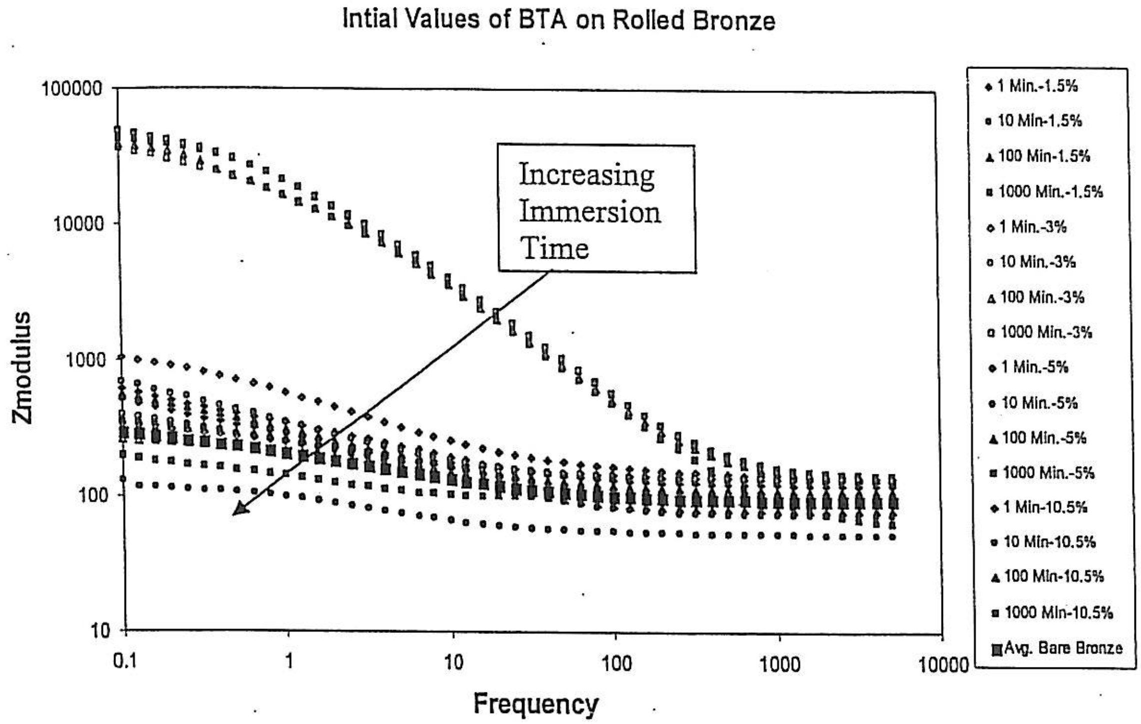


Table 6.Bode Plots at various times of immersion

These plots show that the BTA provides some protection. This graph shows more clearly the added resistance of the BTA film when immersed for longer periods of time.

These results suggest that the immersion time of the BTA solution plays a significant role in the performance of the Cu-BTA coating in corrosion protection. This work indicates that different immersion times and concentrations of BTA/ethanol do provide varying protection. It was found the 3%, 5%, and 10.5% BTA/ethanol solution immersed for longer durations did afford the highest protection to the metal. Unfortunately this model can not be repeated in actual applications because of the nature of the substrate. It is the conclusion of the authors that a BTA pretreatment affords little corrosion protection, when applied in very thin films. Perhaps a system can be developed to increase the time the BTA is in contact with the substrate.

Survey of Practices Used on Outdoor Bronze

Currently underway is the analysis of a web survey, which focuses on the attitudes towards various approaches in outdoor bronze conservation. A letter in the form of an e-mail was sent out to approximately 500 conservators who are listed, as sculpture conservators, in the American Institute of Conservation Directory, participated in the Metals 2001 Conference, or lists themselves in the Conservation Distribution List as working with bronze. Using the survey we will monitor the opinion of conservators throughout the world on the novel ideas we have for this project. We hope to also obtain a broad opinion of the needs of the conservation community. A paper version of the survey can be viewed in Appendix A.

Appendix A

On-line Bronze Conservation Survey

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Note: While taking this survey please try not to hit the enter key, as this will submit only the part of the survey you have completed. If this does happen, hit the "back" button on the internet explorer that you are using to continue with the survey. When you are have completed the survey, please state in the "comments area" if you were forced out prior to finishing the survey, to prevent distorting the data.

1. Have you ever cleaned an outdoor bronze?

- No
- Yes

1a. What materials/tools do you use in cleaning an outdoor bronze?

Please specify:

* Detergent?
* Brushes?
* Water system?

2. Have you ever coated an outdoor bronze? Yes No

3. Have you ever re-patinated a sculpture? Yes No

4. Have you ever used blasting techniques to clean an outdoor bronze?

- No
- Yes

4a. Have you blasted with (Check all that apply):

a. Water

b. Walnut shells

c. Other organic material, please specify

d. Glass beads

e. ☐ Dry Ice
f. ☐ Baking soda
g. ☐ Other, Please specify: ________

4b. Out of 10 sculptures on average, how many would you blast? ____

5. In your opinion, what is the most important feature of a coating?
Please rate the following where 1 is very important and 5 is not important.

	Very Important	<====>			Not Important
	1	2	3	4	5
Longevity	○	○	○	○	○
Ease of application	○	○	○	○	○
Safety	○	○	○	○	○
Appearance	○	○	○	○	○
Weather resistance	○	○	○	○	○
Removeability	○	○	○	○	○
Other, please specify: ____	○	○	○	○	○

6. Have you used a wax coating?

○ No

○ Yes

6a. What waxes have you used (Check all that apply)?

☐ Butcher's Wax

☐ Trewax

☐ Johnson Paste Wax

☐ Renaissance Wax

☐ Other microcrystalline blends

☐ Other, please specify: ________

6b. How have you applied the wax (Check all that apply)?

☐ Brushing

☐ Spraying

- [ ] Cloth application

6c. Is there any application method you find most effective?

- ( ) No
- ( ) Yes
  Please indicate method:
  - ( ) Brushing
  - ( ) Spraying
  - ( ) Cloth application
  - ( ) Other, please specify: [ ]

6d. Have you ever applied a hot wax? ( ) Yes ( ) No

6e. What have you used to buff the wax? (Please indicate tools)

[ ]

6f. On average, how often is the wax reapplied?

- ( ) more often than once a year
- ( ) once a year
- ( ) once every two years
- ( ) once every two + years
- ( ) other [ ]

6g. Have you ever tinted the wax with pigment? ( ) Yes ( ) No

7. Have you used a coating besides wax?

- ( ) No
- ( ) Yes,

7a. Please indicate all coatings and specific brands if possible?

[ ] Incralac (Acryloid B-44)	
[ ] Acryloid B-48	
[ ] Agateen	

Acrylic	
Urethane	
Acrylic/Urethane	
Waterborne acrylic	
Silane based coating	
Other, please specify all	

7b. What features are you looking for in a non-wax coating?

Please specify:

7c. Do you apply a wax coating on top of the non-wax coating?

Yes No

8. Have you ever used a corrosion inhibitor pretreatment (such as benzotriazole BTA) on outdoor bronze?

No

Yes

8a. Was this pretreatment used under wax, or a polymeric coating?

Wax Non-wax coating Both

8b. Please indicate the pretreatment system you use:

BTA (benzotriolazole)

Silane

Other

8c. On average, how often do you re-apply the corrosion inhibitor?

9. Would you use a protective clear coating if it is not removeable by solvents?

Yes

No

9a. If the coating is removable by mechanical means?

- Yes
- No

9b. If the mechanical means did not change the surface of the bronze (such as laser cleaning)?

- Yes
- No

9c. If other methods were developed to remove the coating without changing the surface?

- Yes
- No

10. Would it be valuable to have a coating where the gloss could be adjusted within the coating?

Yes No

11.Do you see a need for a long-term coating system (more than one year) for outdoor bronze?

Yes No

12. What is an appropriate lifetime for a protective coating on bronze?

- 1 year
- 2-5 years
- 5-10 years
- 10 years
- As long as possible

13. Please list any comments or concerns you have with outdoor bronze sculpture or this survey:

Please use the submit button to submit your answers: Submit my answers

Thank you for your time and expertise.

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