NORTH DAKOTA STATE UNIVERSITY

INTERIM REPORT
TO THE
NATIONAL CENTER FOR PRESERVATION TECHNOLOGY AND TRAINING
MT-2210-9-NC-20 GRANT PROGRAM

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

2. Project title: Development and Testing of Organic Coatings for the Preservation of Outdoor Bronze Sculpture from Air-Pollutant Enhanced Corrosion-Year 3

3. Recipient North Dakota State University
   Fargo, ND 58105

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   Fargo, ND 58105

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

3. Grant Number: MT-2210-9-NC-20

4. Dispersion of nanosize TiO2 has been unsuccessful. Attempts are being made to fully disperse the pigment into a clear coat in a one percent concentration, and obtain an optically clear system. Any change of the schedule that this later entails will be communicated to Dr. Mary Striegel.

5. Progress to date through July 5, 2002

FLOUROPOLYMERS

In a search for a coating that would be suitable for an outdoor bronze, initial investigation of a fluoropolymer based on polyvinylidene fluoride (PVDF) looks promising. 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 optically clear.

The PVDF that is being explored is Kynar® RC-10,052 PWD PVDF, made 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 affords very poor adhesion to the bronze substrate, a common problem with fluoropolymer coatings. The chemical inertness of PVDF also makes it difficult to increase its adhesion to metal substrates.[1] To increase adhesion of the PVDF, we have blended the copolymer with an acrylic polymer. The acrylic used is Paraloid B-44, which is an acrylic resin made by Rohm and Haas. This acrylic also happens to be the base for Incralac®, currently the most popular acrylic coating, used by conservators on bronze sculpture. An acrylic was chosen to blend with the copolymers, because of its known properties of refractive index and the ability to remove the acrylic if necessary. The PVDF/acrylic blend has increased adhesion to an average range. We are currently studying another Rohm and Haas acrylic, Paraloid A-21, in hopes of furthering the adhesion of the fluorocarbon.

Initial electrochemical studies indicate that the fluorocarbon-acrylic blend has the potential of being an excellent coating. The following figure, measured initially after the coating was cast over the bronze substrate, demonstrates the initial electrochemical impedance spectroscopy (EIS) results of the blend on rolled bronze. It indicates the greater barrier properties of the fluoropolymer-based coatings.

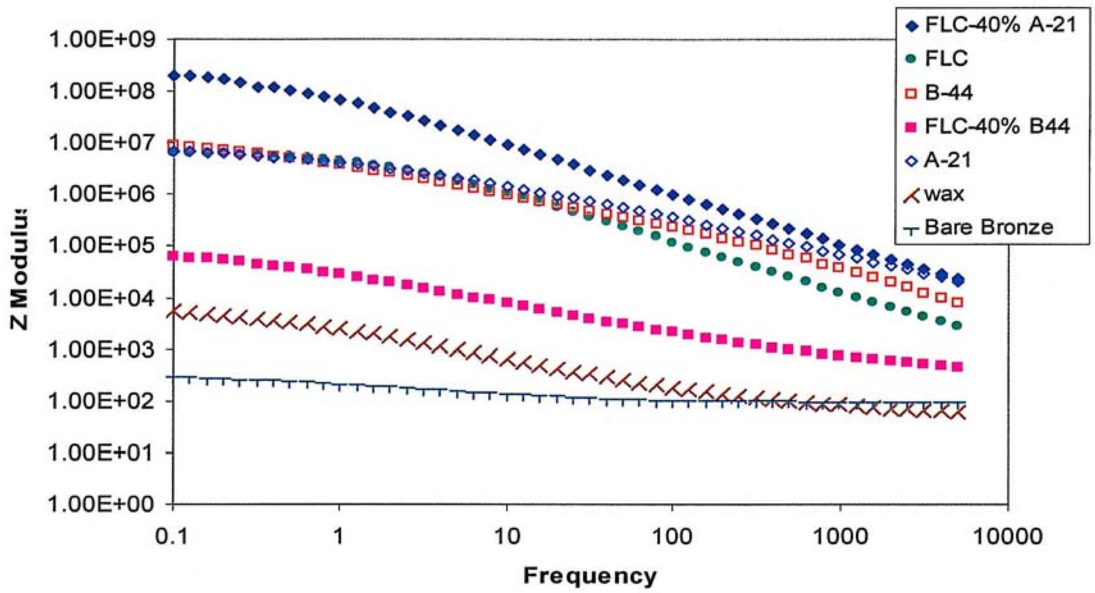


Figure 1. Bode plot of initial impedance values of various protective coatings.

The low frequency portion of this Bode plot, indicate that the PVDF is a very high resistance coating. The authors would like to note the significant difference in resistance between the wax sample and the other tested coatings. Further studies will again look at increasing the adhesion of the coating, along with artificial weathering of the coating on cast bronze.

COMPARITIVE STUDIES OF COATINGS

To identify the weathering of various coatings on two different substrates, a variety of coatings are undergoing an artificial weathering scheme in accordance consisting of Prohesion® and exposure in the QUV® chamber according to ASTM D 5894-96 *Standard Practice for Cyclic Salt Fog/ UV Exposure of Painted Metal, (Alternating Exposures in a Fog/ Dry Cabinet and a UV/ Condensation Cabinet)*. The coatings being studied are listed in Table 1.

	SAMPLE
1	Uncoated polished bronze
2	Uncoated patinated bronze
3	Polished bronze coated with Incralac
4	Patinated Bronze coated with Incralac
5	Polished bronze pretreated with 1% BTA/ethanol solution and coated with Incralac
6	Polished bronze coated with 50:50 8% fluorocarbon/40% Paraloid A-21

Table 1. Sample descriptions

Each sample was made in triplicate on cast polished bronze and French brown patinated bronze.[2] The sample degreasing for cast bronze was as follows:

The samples were placed in a hexane bath for approximately one minute, washed with hexane and wiped clean with using a cotton cloth. The panels were then washed with Acryli-Clean®, wiped clean with a cotton cloth and placed in an acetone bath for one minute. Following the acetone bath the panels were washed with acetone, ethanol and Acryli-Clean®. The panels were wiped clean after each wash with a clean, dry cloth. Those panels that were pretreated with the BTA were placed in a 1.5 % solution of BTA in ethanol for one minute and rinsed with ethanol to remove any residue. The topcoat on the BTA treated panels were miscast two times before an acceptable coating was achieved. In this case the topcoat was removed using acetone and the BTA pretreatment was repeated to ensure an intact pretreatment layer still was in place. As a result the panels were immersed in the 1.5 % ethanol for 3 minutes total.

The sample degreasing of the patinated samples were as follows: The sample was immersed in an acetone bath for 1 minute. The patinated sample was then flooded with acetone, and wiped clean with a cotton cloth. This procedure was repeated using ethanol.

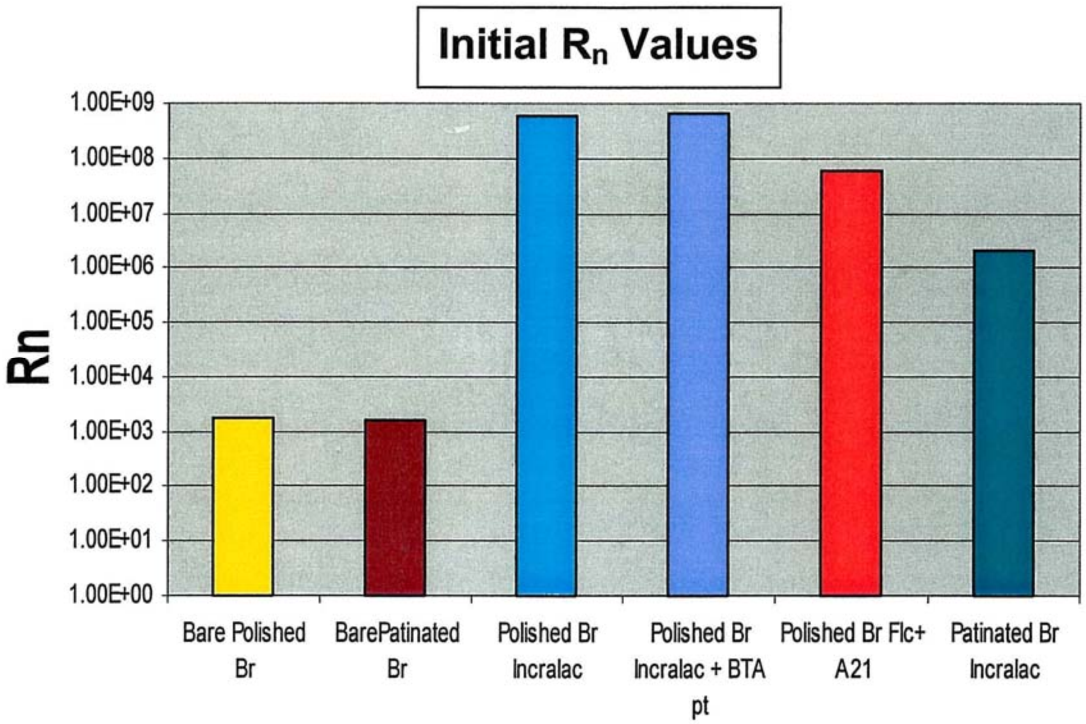
Three samples of each substrate/coating, described in Table 1, were prepared. The samples were coated on a Thomas Scientific 6410-T40 automatic film applicator. The rate of application was 5cm/sec and a 90 micron bar was used.

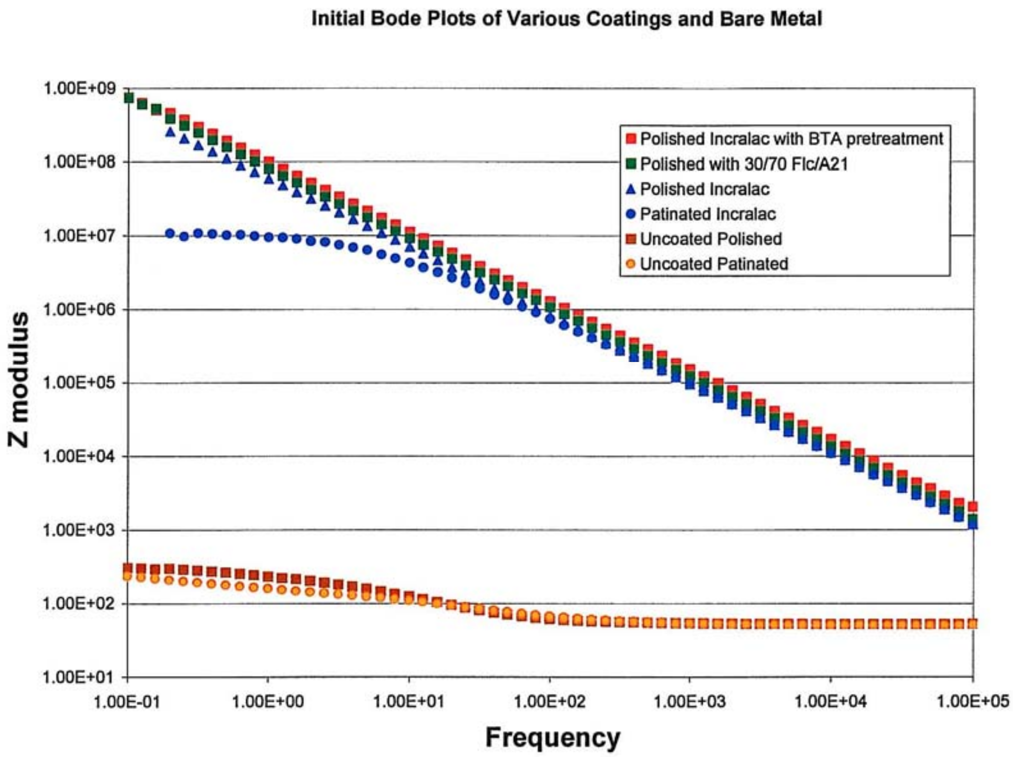
After each set of samples were cast, one sample of each coating was cut in half. This was done so that two nominally identical samples could be obtained for running Electrochemical Noise Monitoring (ECM).

Before weathering, a digital image of each of the samples was obtained using a HP 6300C Scanner at a resolution of 200 pixels/ inch. The average film thickness for each sample was determined using Elcometer 345 thickness gauge for nonferrous metals. The color of each sample was obtained using a Microflash® made by Datacolor International and the L*, a*, b* of each was recorded. The contact angle of each sample was obtained using a dynamic contact angle analyzer, FTA 125. The initial gloss readings were analyzed using Novo-gloss™ Model number made by Gardco® at 20, 60 and 90 degrees. All these physical properties will be monitored throughout the weathering process.

In addition to the physical properties ECN and electrochemical impedance spectroscopy (EIS) is being monitored. The electrochemical cell for the EIS 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. For the ECN, the same o-ring as mentioned above was clamped to two nominally identical panels that were then attached with a salt bridge. A saturated calomel reference electrode was immersed in dilute Harrison's solution in each. Electrochemical noise was measured using a zero resistance ammeter and data logger FAS-1 made by Gamry. Measurements are made every 0.2 second for a period of 1 minute. The current between the two working electrodes is monitored and at the same time the voltage of the pair is measured with respect to the reference electrode. From the resultant data points, the standard deviations of the voltage and current are calculated. This is repeated ten times. By dividing the current between the two working electrodes by the voltage between the two metal substrates, the parameter noise resistance (Rn) is derived. A total of four samples were compared, and the noise between each of the panels was monitored.

Initial averaged noise and impedance results are presented below:





These results show the high impedance of the coated samples. Continual monitoring of the samples as accelerated weathering is continued will occur.

ULTRAVIOLET ABSORBERS

In attempt to monitor the UV absorption of organic and inorganic UV absorbers, various UV absorbers are being studied. Coatings containing the UV absorbers are cast onto both cast bronze and quartz slides. Both substrates will be weathered in a Q-Sun ultra violet chamber. The degradation of the films and UV absorption of the various UV absorbers will be monitored by Atomic Force Microscopy, and UV spectroscopy.

EXPERIMENTAL

Resin Preparation

Seven different resins, all containing Paraloid® B-44S, are being prepared by adding various UV absorbers (UVA's) and/or hindered amine light stabilizers (HALS). The various formulations used in the study are summarized in Table 1.

Table 1. Resin formulations

Resin	Formulation	Comments
B44	B-44S	B44-S is an acrylic copolymer comprised of methyl methacrylate and ethyl methacrylate in toluene. The solids content is 40%.
B44 and BTA	1% BTA in B44-S	Benzotriazole (BTA) is a solid UVA
B44 and Tinuvin® 5050	1% (by weight) Tinuvin® 5050 in B44-S	Tinuvin® 5050 is a liquid UVA/ HALS
B44 and TiO_2		TiO_2 is an inorganic UVA
B44 and ZnO_2		ZnO_2 is an inorganic UVA
B44 and Carbon Black		Carbon Black is a UVA
B44, BTA and Tinuvin® 5050	0.5% BTA and 0.5% (by weight) Tinuvin® in B44-S	

The B44-S polymer used to prepare the resins was obtained from Rohm and Haas. The BTA, the Tinuvin® 5050 and the TiO_2 (VV-Titan) was obtained from Aldrich Chemical Company, Ciba Specialty Chemicals and Kemira Pigments, respectively. The formulation with BTA, Tinuvin, and the combination of the two were easily dispersed into the B-44. We are currently having problems fully dispersing the nanosize pigment particles into the clear coating to achieve a clear resin. The following describes the processes that have been attempted.

TiO_2 DISPERSION

Various methods and dispersants were used, unsuccessfully, to disperse the TiO_2 in the Paraloid® B44 resin. Initially, dispersant was added to the resin followed by the addition of the pigment, during which time, shear was applied to the mixture via a cowls blade attached to a high speed disperser. Mechanical dispersion using glass beads, a sonic bath and mechanized rollers were also unsuccessful in dispersing the TiO_2.

Most of the attempts at dispersion involved making a paste of TiO_2 and dispersant. A mortar and pestle were used to provide mechanical energy to the system. The paste was then added to Paraloid® B44 resin to give a 1% mixture of TiO_2/B44+dispersant. Shear was applied to the mixture using one of the mechanical dispersion methods described above.

The ratio of pigment to dispersant as well as the brand and type of dispersant were varied. The dispersants used in the experiment were obtained from EFKA and BYK-Chemie. The dispersants used were: EFKA 5010, DisperByk 112, DisperByk 142, DisperByk 163 and DisperByk 2001.

We are exploring various methods using a sand mill, and dispersing using a Sol-ge1 method.

SUBSTRATE PREPARATION

Bronze panels, consisting of 85% copper, 5% zinc, 5% tin and 5% lead, were prepared in three steps. The panels were sanded with 600, 1500, 2400, 3600, 4000, 8000 and 12000 grit sand paper. Next the panels were cut into 1cm x 1cm squares on a wet saw with a diamond blade. The bronze substrates were polished with three successively finer grades of alumina micropolish (1.0, 0.1 and 0.05 respectively) obtained from Union Carbide.

COATING PROCESS

The bronze substrates were coated on a WS-200-4NPP/RV spin coater from Laurell Technologies Corporation. The substrate was vacuum sealed to a rotating disk and the resin was applied dropwise to the spinning bronze substrate. Rates of rotation were varied (1800 to 4500 rpm) based upon the viscosity of the resins. The coated substrate was spun for an additional two minutes after the resin was applied to provide complete coverage of the prepared substrate surface and to allow for the formation of a uniform coating.

UV-VIS SPECTROMETRY

A 75μm film of each resin (see Tablel) was cast onto a 50mm x 25mm quartz slide. The absorption spectrum of the samples, from 500nm to 175nm, was obtained on a Cary Varian UV-vis Spectrophotometer and processed on a Sun Microsystems workstation.

BRONZE SURVEY RESULTS

The techniques and materials used to conserve and protect outdoor sculpture are as varied as the sculpture being treated. As part of a larger study in protective coatings for outdoor sculpture and ornamentation, funded by the National Center for Preservation Technology and Training, an on-line survey, focusing on the techniques used on outdoor bronze, was conducted. The survey compiled a list of maintenance procedures, and the materials used by the participating conservators. In addition, the surveyed conservators provided a targeted outline for properties of an *ideal* outdoor bronze coating. Results of this study will help us to better develop new coating systems for outdoor bronze conservation. Findings of the survey as well as potential new coating systems will be discussed. (See Appendix A)

6. The specific issues facing us that need to be resolved are obtaining proper or improved dispersion of the nano-sized TiO_2, improving the adhesion and use of the fluoropolymer based clear-coat, and developing a plan for acquiring or synthesizing polymers with "tuanable" removability. We are addressing these issues as time allows.
7. CHANGES IN OBJECTIVE, BUDGET, OR PRODUCTS – No changes are anticipated.
8. The final work for this project is scheduled as:

   July-August 2002. Continuous electrochemical, physical and chemical testing on samples. Will look to include new polyurethane coatings to the series of samples being weathered. Continue to attempt to disperse nanosize TiO_2 particles into the clear coat, Paraloid B-44

September 2002. Make further analyses of cyclic testing + electrochemical testing results. Write Final Report

9. Reports, presentations, and publications are the primary products of the project at this time. In the Appendix, we attach our new papers to date.
10. Products:

"On-line Survey Results of Techniques used for Outdoor Bronze Conservation" Presented as a paper and as an oral presentation at the AIC 2002 Conference in Miami, Fl. (Appendix A)

"Developing and Testing a New Generation of Protective Coatings for Outdoor Bronze Sculpture" Presented as a paper and as an oral presentation at the 2002 Athens Conference on Coatings Science and Technology, Vouliagmeni (Athens), Greece. (Appendix B)

REFERENCES

1. Iezzi, Robert, Scott Gaboury and Kurt Wood, (2000) "Acrylic-fluoropolymer mixtures and their use in Coating" *Progress in Organic Coatings*, 40, 55-60.
2. Bierwagen, G., Tara Shedlosky, Kimberly Stanek "Development and Testing of Organic Coatings for the Protection of Outdoor Bronze from Air-Pollutant Enhanced Corrosion- Year 1 and 2." Final report to the NCPTT 1999 and 2000 grant Program.

APPENDIX A

On-line Survey Results of Techniques used for Outdoor Bronze Conservation

Tara J Shedlosky, Kimberly M Stanek and Gordon Bierwagen
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ABSTRACT

The techniques and materials used to conserve and protect outdoor sculpture are as varied as the sculpture being treated. As part of a larger study in protective coatings for outdoor sculpture and ornamentation, funded by the National Center for Preservation Technology and Training, an on-line survey, focusing on the techniques used on outdoor bronze, was conducted. The survey compiled a list of maintenance procedures, and the materials used by the participating conservators. In addition, the surveyed conservators provided a targeted outline for properties of an *ideal* outdoor bronze coating. Results of this study will help us to better develop new coating systems for outdoor bronze conservation. Findings of the survey as well as potential new coating systems will be discussed.

INTRODUCTION

A survey on the methods and materials used by outdoor bronze conservators was conducted to obtain a broad opinion of both practical information about the techniques and materials used to maintain outdoor sculptures and the future needs of the conservation community relating to coatings for outdoor bronze sculpture. Through this survey we hoped to develop specifications for formulating coatings for outdoor bronze which the authors of this paper will attempt to apply to nove1 coating ideas for outdoor bronze conservation.

The survey was conducted on-line to insure anonymity in the responses, as some of the questions could be interpreted as ethically challenging. The cost of addressing people on line was a more efficient use of time and funds verses sending out mass mailings to conservators. In addition, contacting people on-line allowed to easily communicate with conservators throughout the world.

A letter in the form of an e-mail was sent out to approximately 500 conservators including: sculpture conservators from the AIC Directory, people who participated in the Metals 2001 Conference, people on the Conservation On-line Distribution List (CoOL) who listed themselves as working with bronze. In addition a request was posted on the CoOL. The letter included a password to enter the on-line survey to ensure only the targeted conservators would be able to fill out the survey. The entered data was stored on a controlled spreadsheet. This made the process efficient, avoiding having to reenter the results.

A total of 38 people answered the survey. Although this seems like a low percentage of participants, the following statistic indicate that those who did respond are very important to the preservation of bronze objects. Of these responders, 95% had cleaned, 87% had coated and 58% had repatinated an outdoor bronze. These statistics indicate that the people responding to the survey have relevant backgrounds that represent true practices of outdoor bronze conservation and maintenance. Throughout the remainder of this paper, these respondents will be referred to as the "conservators".

SURVEY RESULTS

Cleaning

When asked about the materials used to clean outdoor bronze, of the conservators asked, 40% use nylon brushes or scrub pads and 51% use natural brushes. The following chart represents the different detergents reportedly used by conservators and the percentage of conservators that report using each detergent.

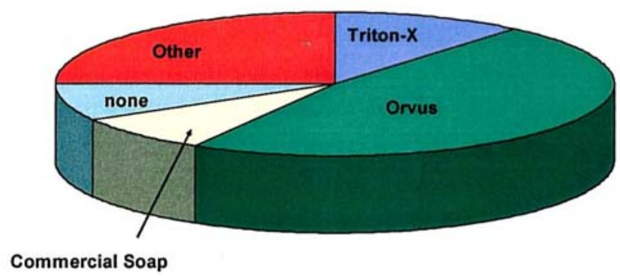

Figure 1. Different types of detergents used by conservators

Triton-X™ (was a registered trademark formerly owned by Rohm and Haas Co., but now owned by Union Carbide) is a nonionic detergent. The "X" series of Triton detergents are produced from octylphenol polymerized with ethylene oxide. Orvus® WA Paste is produced by Proctor and Gamble it is reportedly an extremely gentle detergent designed to clean cattle and horses. In the "other" category detergents that are used are Vulpex, Teric 90, and the surfactant Synperonic N. Ivory® dish detergent was also reportedly used.

Blasting is sometime used to remove unwanted films and clean items. It was reported that 44 % of the conservators had used this technique to clean a bronze sculpture about 1.5 % of the time. The following graph represents the different materials used to blast sculptures and the number of conservators reportedly using them.

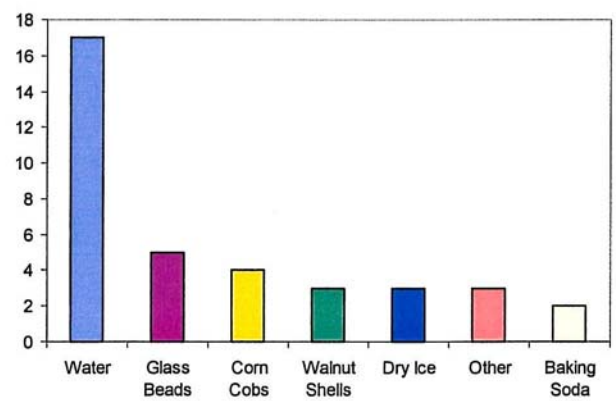

Figure 2. Blasting Media used to clean bronze sculptures.

Coatings

Atmospheric corrosion is becoming more prevalent throughout the world and results from 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. Protection from bronze corrosion is thus very important when trying to conserve bronze sculpture situated in a hostile environment. In attempting to maintain the original intent of the artist one must protect the bronze with the least intrusive means possible. The primary method of protecting bronze from elements found outdoors is using a protective coating. In developing a protective coating it is important to understand what is wanted and needed by the conservation community.

The surveyed conservators were asked to rate various potential properties of a coating on a sliding scale and report where the feature lay between very important and not important. The following figure graphically represents the results.

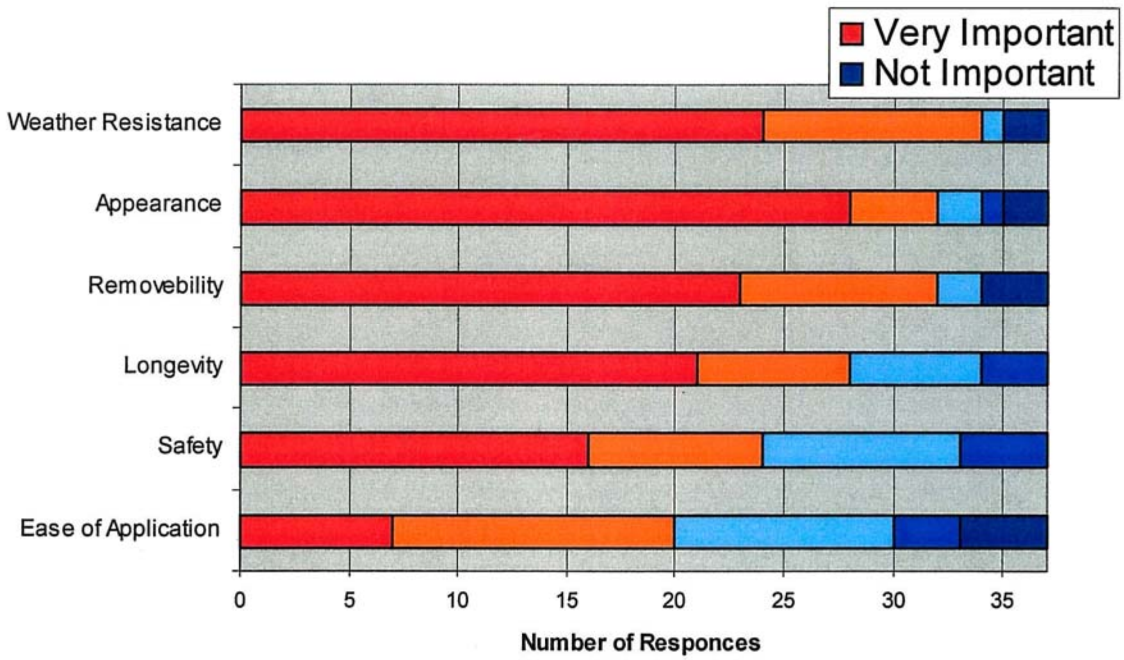

Figure 3. Coating features rated on a sliding scale.

The above results indicate that the three most significant features to build into a coating are weather resistance, the appearance of a coating on a bronze and the ability of a coating to be removable. The three other features as well are indicated as important to a majority of the surveyed. It was pointed out in the comments section of the survey that cost and availability of the coating system are issues that also must be addressed.

Wax

Wax is by far the most popular coating system used on outdoor bronzes. Wax is assumed to be protective, and fully removable. Although comments from a surveyed conservator say, "...wax can build up and change the appearance from multi-colored to a thick and glossy uniform brown. Further, it is very difficult to remove a wax coating and raised areas of bronze on the surface still become worn down and turn green. The wax can also assist harmful materials such as stray fertilizer pellets, in damaging the surface of the bronze by eating through via small openings and spreading under the layers of wax." Never less, wax is a cost effective material and is easily applied and thus readily used. This same conservator went on to say that, "most curators and museum visitors, etc. aren't bothered by the change in appearance. Like so many (preventive) conservation treatments, protective wax coatings seem more beneficial than most other coatings at this time." The survey results indicate the popularity of wax, as 92% of the surveyed conservators have applied wax coatings. Brushing and Cloth applications of wax are the most popular, only 9% had used spraying methods to apply the wax. Application of a hot wax technique was used by 62% of the surveyed and 70% of conservators have tinted the wax. The graph below in *Figure 4* represents the average wax reapplication.

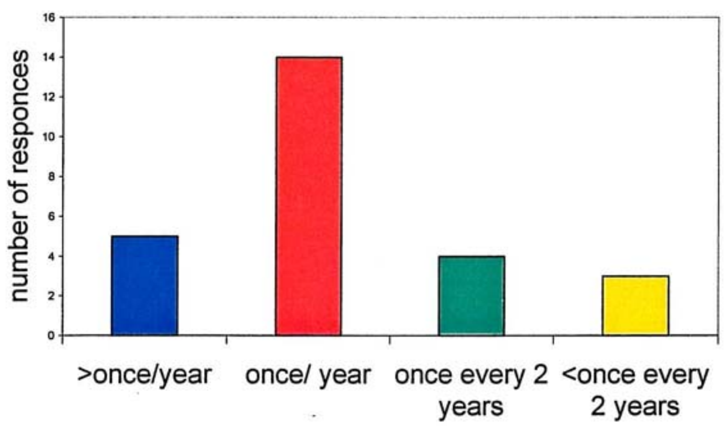

Figure 4. Average wax reapplication.

Typically wax is applied once per year. It was pointed out by a conservator that, "post-conservation maintenance of outdoor sculpture is often the responsibility of the institutional owner" and therefore out of control of the conservator. The following figure graphically represents the types of waxes and their frequency of use by conservators.

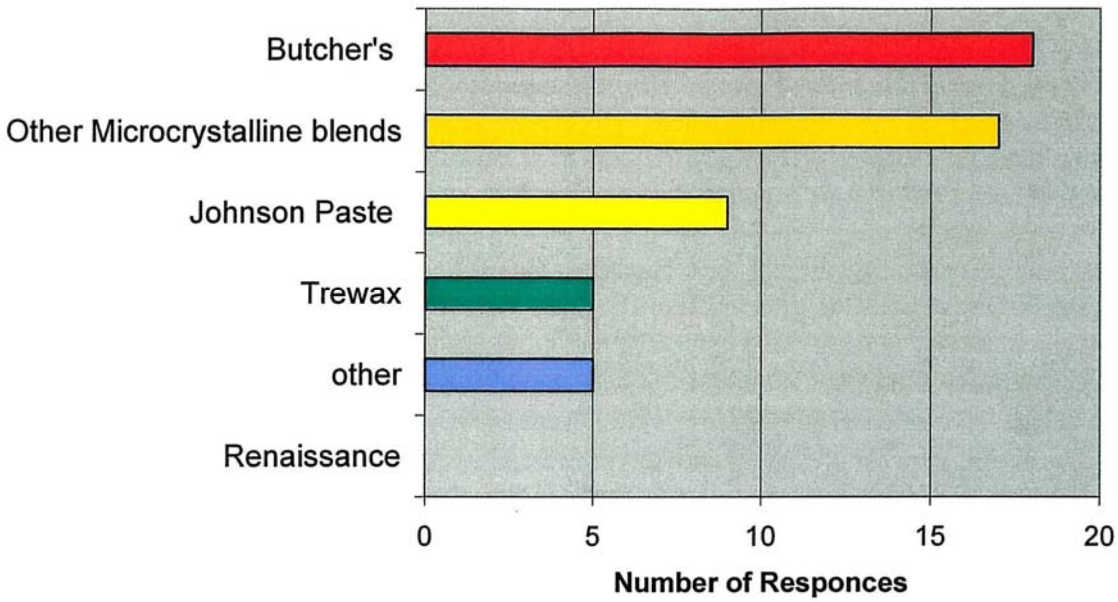

Figure 5. Types of Waxes and frequency of use.

Butcher's bowling-alley-paste wax, which is a carnauba wax, natural and synthetic waxes in mineral spirits and turpentine (or other hydrocarbon) [1], is the most popular type of wax. The microcrystalline blends are also commonly used and are often mixed by the conservator. Other waxes that were reported to be used are carnauba blends and synthetic beeswax.

Pretreatments

Corrosion inhibitors retard the formation of corrosion through complex mechanisms, which are often more than simple barrier properties. The inhibitors suppress either the cathodic or anodic or both electrochemical reactions. In the case of benzotriazole (BTA), the molecule is chemisorbed on the metal substrate. This chemisorption is facilitated by the polar nitrogen molecules. [2] A total of 57 % of the surveyed conservators, have used a corrosion inhibitor, all report the corrosion inhibitor used as BTA. BTA pretreatments were used under both wax and non-wax coatings.

Non-wax Coatings

Synthetic resins are used to protect bronze instead of using a wax coating. The conservators report that 73% have used a non-wax coating. 90% of the conservators would find it valuable to be able to adjust the gloss of the system. The following figure represents the different coatings that are used and number of conservators who use each.

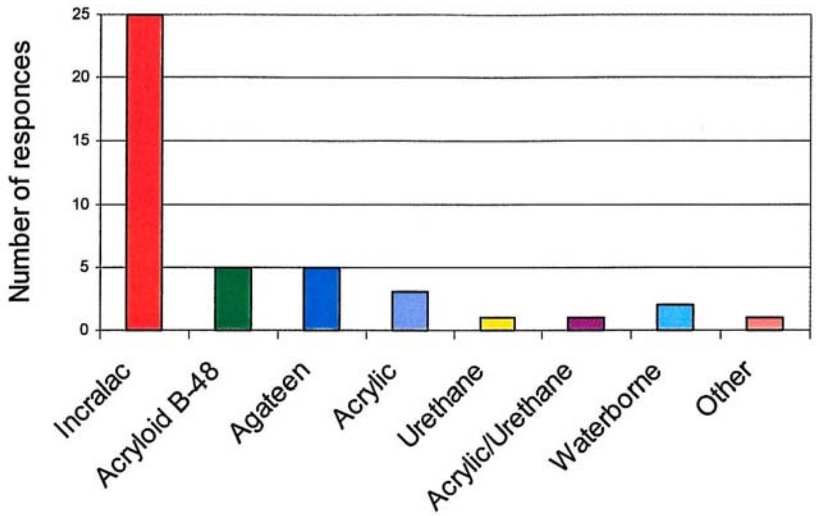

Figure 6. Types of resins that are used on outdoor bronze.

Incralac® is the most popular resin used to protect outdoor bronzes. Incralac® is an acrylic polymer based coating that is solvable in toluene, while the wax is also considered removable. Incralac® was developed in the 1960s by the International Copper Research and Development Corporation in New York. [1] The base of Incralac is the resin Paraloid B-44 made by Rohm and Hass Inc, which is a ethyl methacrylate/methyl methacrylate copolymer. In addition to Paraloid B-44, Incralac® contains a leveling agent, epoxidized soybean oil, an ultraviolet stabilizer – benzotriazole (BTA), toluene and ethanol. BTA also functions as a corrosion inhibitor for the copper in the bronze and is present in the formulation. There have been several studies that have looked at the effectiveness of Incralac® and the conclusions of these studies indicate that Incralac® is an effective coating varying from 16 months to 5 years of outdoor exposure. [1,3,4,5,6,and 7] Thus every 2-5 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 better coating system to replace the Incralac® + wax system.

New Coating Systems

The conservation community on a whole agrees that research needs to be continued to develop polymer coatings for the protection of outdoor bronze sculptures. [1] In attempting to develop a coating for outdoor sculpture, it is important to the authors to understand what type of coating would be accepted by the conservation community. The following statements refer to a fictional coating that would perform better than what is currently available. If a protective clear coating was developed and it was not removable by solvents 29% of the surveyed conservators would use it. If the same coat was removable by mechanical means 31% would use it. If the means did not change the surface 63% would use it. If a different method was developed for removing the coating, without changing the surface 87% would use the coating. When asked about the need for a long term coating system, which was defined as longer that one year, 92% said there was a need for a long-term coating system. *Figure 7* represents the lifetime specifications for a mode1 coating system as defined by the conservators.

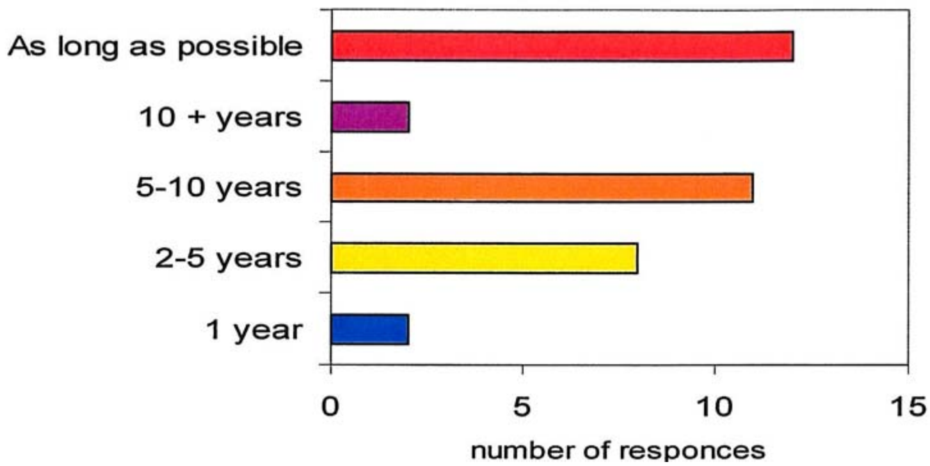

Figure 7. Lifetime Specifications for a model coating system as dictated by the surveyed conservators.

There seems to be a need for a long term protective system, especially if it is removable by a novel technique that does not disturb the surface. There was some concern that if a long term coating system were developed, annual inspections would not be upheld by the owners of the bronze.

The following represents the coating specifications of an *ideal* coating system, as defined by the survey questions and the comments that were submitted to the survey. The coatings must have the following characteristics:

- Protective against corrosion formation (provides a barrier against water, O_2 , or ions)
- Clear (must be able to conform to the optical properties as the conservator and curators sees fit, gloss adjustable)
- Removable
- Easy to apply
- Non-toxic (as little as possible)
- Durable
- Not Degraded by ultra violet light
- Cost effective

CURRENT RESEARCH

This research was recently reported at the 2002 Athens Conference on Coating Science and Technology.[8] For a more in depth analysis, please refer to the references. A fluoropolymer is being studied as a protective coating on bronze when blended with an acrylic polymer. The acrylic used is Paraloid B-44, which is an acrylic resin made by Rohm and Haas. This acrylic also happens to be the base for Incralac®. We are currently studying another Rohm and Haas acrylic, Paraloid A-21, in hopes of furthering the adhesion of the fluorocarbon.

Electrochemical methods such as electrochemical impedance spectroscopy are techniques that provide a quantitative analysis of a corroding material. [9,10] Electrochemical impedance spectroscopy (EIS) is one of the electrochemical methods that can be utilized to characterize the corrosion protection of coatings. [11,12,13] As the corrosion protection of the coating decreases so does the impedance. An increased amount of electrolyte penetrating into the coating is indicative of poor corrosion protection and increases the capacitance of the system. 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 following is a Bode Plot of various coatings on bronze before any weathering occurred.

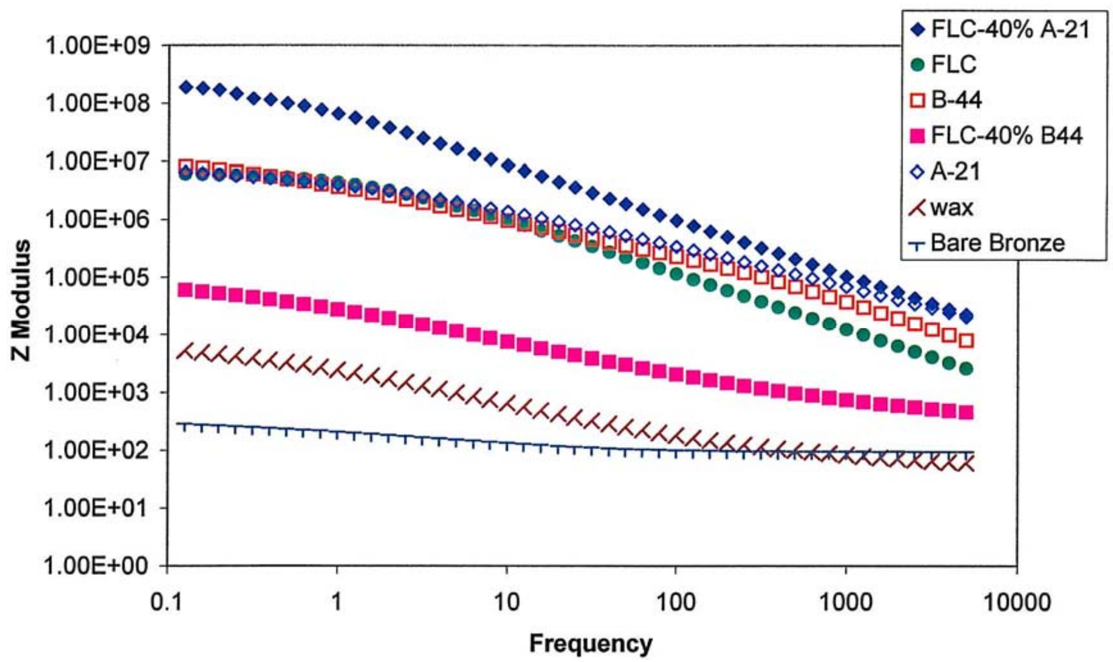

Figure 8. Bode plot of various coatings on bronze, at time zero.

Initial electrochemical studies indicate that the fluorocarbon-acrylic blend has the potential of being an excellent coating. The following figure, measured initially after the coating was cast over the bronze substrate, demonstrates the initial electrochemical impedance spectroscopy (EIS) results of the blend on rolled bronze. It indicates the greater barrier properties of the fluoropolymer-based coatings. The low frequency portion of this Bode plot, indicate that the fluoropolymer-acrylic blend is highly resistant coating. The authors would like to note the significant difference in resistance between that of the wax and the resistance of the acrylic and acrylic blends at low frequencies, even before weathering has occurred. Further studies will again look at increasing the adhesion of the coating, along with artificial weathering of the coating on cast bronze.

CONCLUSIONS

Through this on-line survey, a general overview of materials and methods used in outdoor bronze conservation was obtained. It was found that there seems to be a need for a long term protective system, especially if it is removable by a novel technique that does not disturb the surface. Coating specifications were generated as a goal when developing an ideal coating system. Initial results indicate that there is potentially a significant area of growth in coating systems.

ACKNOWLEDGEMENTS

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APPENDIX B

Developing and Testing a New Generation of Protective Coatings for Outdoor Bronze Sculpture

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Abstract: Outdoor bronze sculpture is vulnerable to acid rain-induced corrosion and the present protection schemes utilized by conservators do not provide adequate protection under many circumstances. To replace the current most common clear bronze protection systems, wax or Incralac® with a top coat of wax, work is underway to develop different options for conservators that include new longer-lasting, more durable systems having improved corrosion protection. The use of improved matrix binders based on fluorocarbon polymers, the use of nano-sized TiO_2 for UV absorption, and the extended use of UVA's and HALS are under examination in a search for improved UV resistance and longer lived corrosion protection in clear bronze coatings. Advanced spectroscopic methods and electrochemical methods are being used to characterize the new coatings candidates with respect to UV resistance and corrosion resistance.

INTRODUCTION

Bronze is one of the most popular materials used in outdoor bronze sculptures. Sculptures placed outdoors are exposed to numerous pollutants and hostile environments. For the most part, outdoor sculptures are left to exist as best they can in their environment. Upkeep of outdoor sculpture is often difficult as funds for maintenance are limited, as well as the quixotic notion of the public that sculpture should age (and change) gracefully with time. Harmful corrosion is often accepted by those who do not understand its consequences. In reality, outdoor sculptures that are exposed to chemical pollution which catalyzes nature's natural threats of moisture, heat, oxygen, ultraviolet, and biological attack to cause irrevocable change from damaging and scarring corrosion.

Atmospheric corrosion is becoming more prevalent throughout the world and results from 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 H2O occurs. Multiple parameters affect the severity of atmospheric corrosion that include: temperature, local atmospheric rain pH, corrosion products, passive film formation, electrolyte thickness, and metal composition. 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 bronze sculpture situated in a hostile environment. Bronze is corroded by atmospheric acids and forms a green and black patina on the surface of the bronze. 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.[2] The corrosion can result is a loss of original patina, and loss of sculptural detail. 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 protective of the bronze by inhibiting corrosion.

The results of this research will be applied to both polished (shiny) bronze, and artificially or naturally patinated bronze. In the truest sense, a patina is a layer of corrosion on the surface of an object. When referring to a bronze object, corrosion and patina have slightly different meanings. As defined by Scott,[3] a patina is "a smooth, continuous layer that preserves detail and shape", he goes onto explain that corrosion can be distinguished from a patina, as corrosion can be defined as "mineral deposits that do not form a continuous and smooth layer". Scott does admit that there is some ambiguity in the terms and goes on to say that "one person's patina..., may be another person's corrosion". In the field of bronze objects, patinas can develop naturally from exposure to the natural environment, or the metal could be artificially *patinated*. When an object has a layer of artificial patina, the metal has been treated with chemicals that react with the metal surface and, most of the time, heat, to result in one of a myriad of colored finishes. In most cases, a conservator is asked to maintain the patina, whether it is natural or artificial.

To slow the aging process while retaining the original appearance of the object, a variety of transparent protective coatings are being used in the field of outdoor bronze conservation.[3] Recently, there have been several studies evaluating different coatings' protective properties on outdoor bronzes in both accelerated and natural weathering.[4,5,6,7] These studies indicate that a tough coating with good adhesion will provide the best resistance to the detrimental effects of weathering on the bronze objects.

When a conservator works with a piece of artwork there are a certain code of ethics maintained. The challenge presented by the conservation community is that every treatment applied to a piece of artwork must be *reversible*. Unfortunately, good adhesion means *irreversibility* for the conservator. In the case of a coating on bronze sculpture, this means that all applied coatings need to be removable without damaging or changing the visible appearance of the sculpture. Although the primary coating used on bronze sculpture is wax[8], previous studies[3,4] have shown more tenacious, less impervious coatings provide better protection. The current procedure is to only apply coatings that are removable by solvents, as non-removable coatings have been interpreted as "adversely (effecting) cultural property or its future."[9] This procedure limits the materials that may be used on a sculpture to thermoplastic, soluble coatings. It has been found in previous studies, various coatings that are not removable with solvents outperform, in terms of coating protection and lifetime of the coating, those that are soluble.[3] This is true because insolubility after film formation usually means chemical crosslinking during the film formation process which leads to a high performance system, as was true in the works cited above.

Coatings provide a barrier between the corrodants and the metal substrate. By various mechanisms the coating system inhibits corrosion. Currently, coatings that are used on outdoor bronzes are overwhelmingly dominated by the use of a thin layer of wax, or an acrylic based coating, Incralac®. These two topcoats are used because they are clear, have good adhesion to the bronze, and do afford some protection to the bronze. But, the main reason they are used is because the two coatings are removable. Incralac® is an acrylic polymer based coating that is solvable in toluene, while the wax is also considered removable. Incralac® was developed in the 1960s by the International Copper Research and Development Corporation in New York10. The base of Incralac® is the resin Paraloid B-44 made by Rohm and Hass Inc, which is a ethyl methacrylate/methyl methacrylate copolymer. In addition to Paraloid B-44, Incralac® contains a leveling agent, epoxidized soybean oil, an ultraviolet stabilizer – benzotriazole (BTA), toluene and ethanol. BTA also functions as a corrosion inhibitor for the copper in the bronze and is present in the formulation. Incralac® + wax has proven to be a better coating system compared to the weathering of the most common use of wax. Incralac® has proven to have limitations. Incralac® is difficult to apply, requires toxic solvents to remove, and its lifetime ranges from 3-5 years.[11] There have been several studies that have looked at the effectiveness of Incralac® and the conclusions of these studies indicate that Incralac® is an effective coating varying from 16 months to 3 years of outdoor exposure.[2,3,4,5] 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 better coating system to replace the Incralac® + wax system. 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 removing and reapplication steps.

In this paper, different methods of protection of a bronze substrate will be discussed, including proposed methods of evaluation and novel ideas specifically designed for outdoor bronze. The topics discussed will include the effect of the substrate treatment, the polymer coating, the pretreatment, and testing of coating performance.

SUBSTRATES

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. This is one of the most common compositions of bronze cast in the nineteenth century used in outdoor statuary found in the US. One hundred 4' x 6' samples were sand cast, with 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. A portion of the panels were treated with a French brown patina. The process used to patinate these panels 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 is rubbed back 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 an 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 was 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.

EVALUATION:

Electrochemical methods such as electrochemical impedance spectroscopy are techniques that provide a quantitative analysis of a corroding material.[12,13] Electrochemical impedance spectroscopy (EIS) is one of the electrochemical methods that can be utilized to characterize the corrosion protection of coatings.[14,15,16,17,18,19] As the corrosion protection of the coating decreases so does the impedance. 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.

FLOUROPOLYMERS

In a search for a coating that would be suitable for an outdoor bronze, initial investigation of a fluoropolymer based on polyvinylidene fluoride (PVDF) looks promising. 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 optically clear.

The PVDF that is being explored is Kynar® RC-10,052 PWD PVDF, made 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 affords very poor adhesion to the bronze substrate, a common problem with fluoropolymer coatings. The chemical inertness of PVDF also makes it difficult to increase its adhesion to metal substrates.[20] To increase adhesion of the PVDF, we have blended the copolymer with an acrylic polymer. The acrylic used is Paraloid B-44, which is an acrylic resin made by Rohm and Haas. This acrylic also happens to be the base for Incralac , currently the most popular acrylic coating, used by conservators on bronze sculpture. An acrylic was chosen to blend with the copolymers, because of its known properties of refractive index and the ability to remove the acrylic if necessary. The PVDF/acrylic blend has increased adhesion to an average range. We are currently studying another Rohm and Haas acrylic, Paraloid A-21, in hopes of furthering the adhesion of the fluorocarbon.

Initial electrochemical studies indicate that the fluorocarbon-acrylic blend has the potential of being an excellent coating. The following figure, measured initially after the coating was cast over the bronze substrate, demonstrates the initial electrochemical impedance spectroscopy (EIS) results of the blend on rolled bronze. It indicates the greater barrier properties of the fluoropolymer-based coatings.

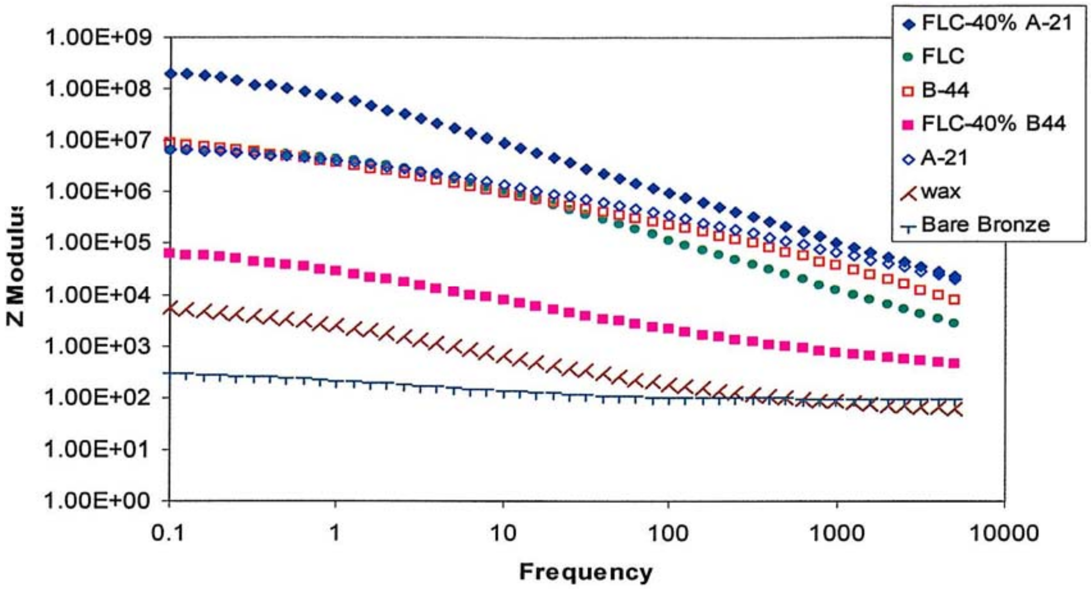

Figure 1. Bode plot of initial impedance values of various protective

The low frequency portion of this Bode plot, indicate that the PVDF is a very high resistance coating. The authors would like to note the significant difference in resistance between Further studies will again look at increasing 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. Conductive polymers have been shown to provide excellent to poor protection for metals.[21] Because of their conductive properties, most of the polymers are not optically transparent. There are a very few references to optically clear conductive polymers.[2,23,24,25] The references indicated that the optically clear conductive materials are difficult to use. The fact that most conductive polymers display opacity and color does not meet the requirement for use with bronzes that were cast with no colored coating used by the original sculptor. Nevertheless, because of the protective properties of the conductive polymers on aluminum, the conductive polymer, poly(3-octylpyrrole) (POP) was studied on cast bronze. It was felt that if the conductive polymer coating provided some protection in an opaque, colored state, it would be worthwhile to then pursue an optically clear system. The POP with two different dopants were studied. The first has the dopant, para-toluenesulfonate (pTS) and the second had pTS and sodium perchlorate (ClO_4). The conductive polymers were dissolved in a 50/50 solution of 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 coating was 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 samples can be viewed in Figures 2-4.

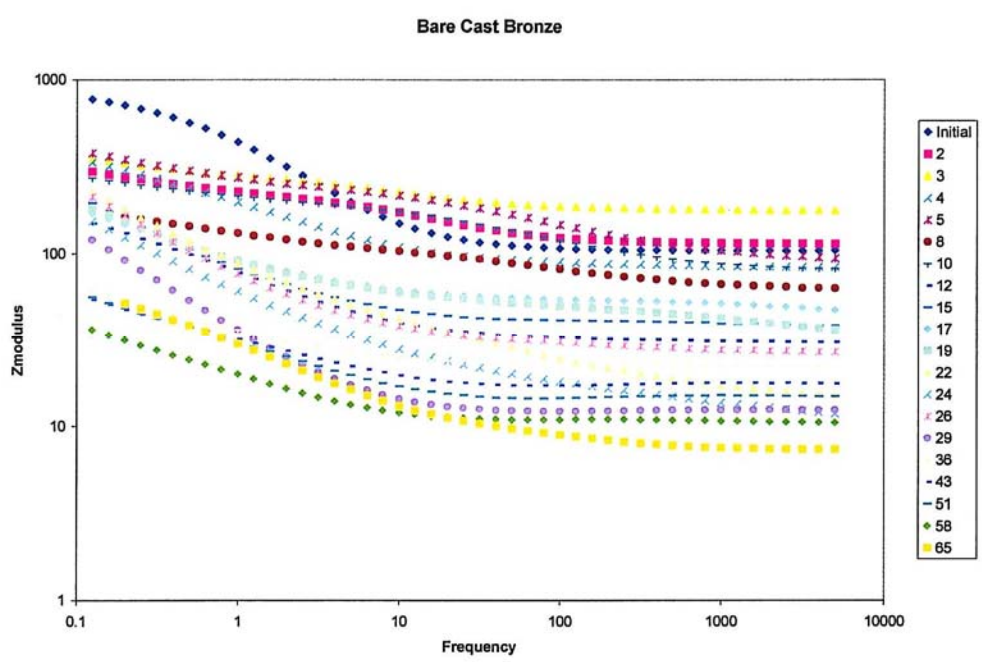

Figure 2. Bode Plots Uncoated Cast Bronze at Various Exposure Times

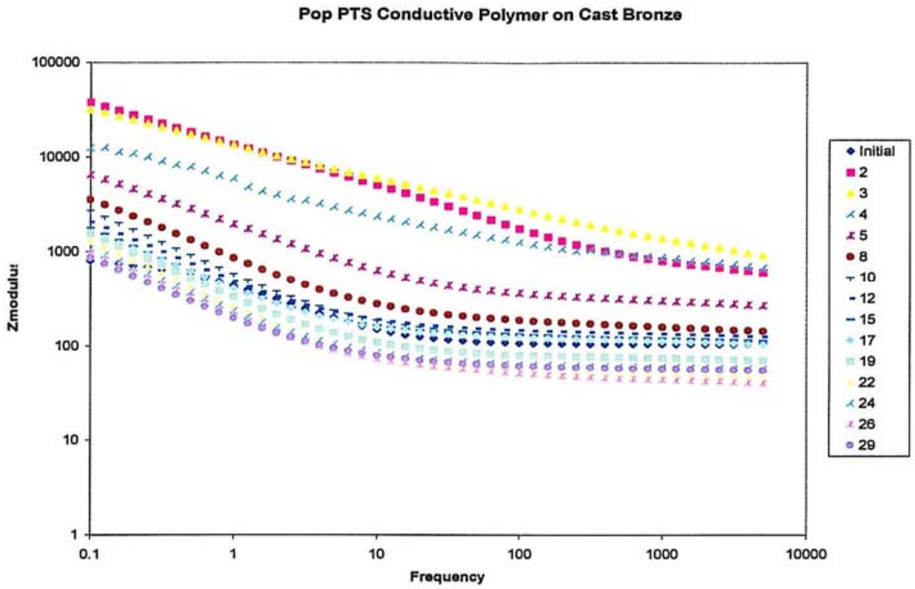

Figure 3. Bode Plots for PTS —Doped POP over Cast Bronze at Various Exposure times

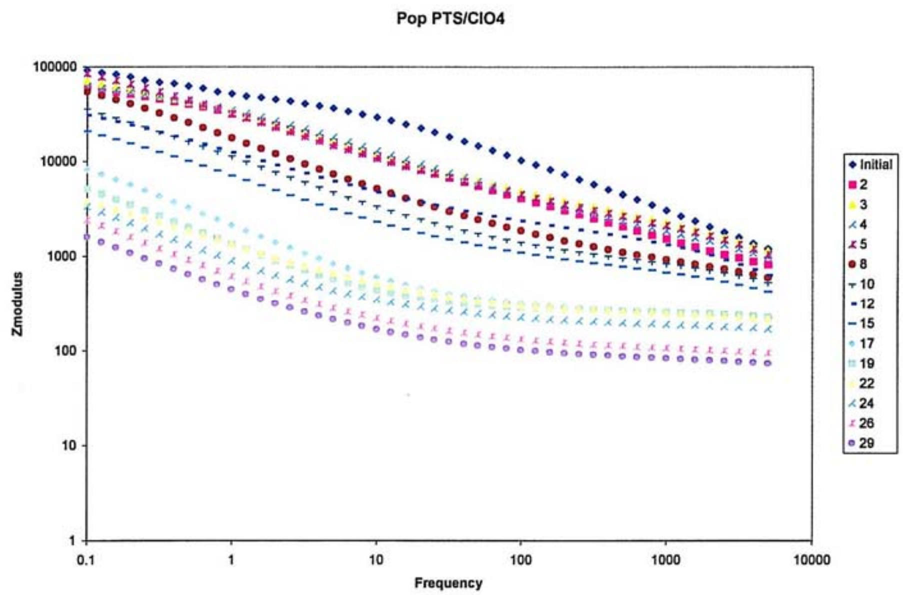

Figure 4. Bode Plots for PTS/Perchlorate—Doped POP over Cast Bronze at Various Exposure times

The two conductive polymers provided protection for the bronze for 29 days, when 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. The conductive polymers because of their unique optical properties have the potential of being used as patination materials, which would provide corrosion protection to the substrate.

BTA PRETREATMENTS

BTA has been used as a coating to prevent both atmospheric and underwater corrosion of copper.[26] Since the 1960's object conservators have used BTA as a treatment on copper and copper alloys to prevent "Bronze Disease". Bronze Disease is an unstable pale green corrosion product which forms when cuprous chloride is converted to cupric chloride.[27] BTA was used as a pretreatment for outdoor bronze sculptures in a variety of concentrations and solvents. BTA forms a complex with Cu(I) and Cu(II) and thus forms a very thin protective film. A recent study looked at Cu-BTA films using reflection-absorption infrared spectroscopy.[28] The study showed the film thicknesses of the Cu-BTA layer generally increases linearly with time of immersion, and that the growth rate is dependent on the concentration. This topic was researched to see if an improved method of use BTA existed for outdoor bronze protection.

BTA has been used for years to stabilize objects housed indoors, but is now also being applied on outdoor sculpture. Although many empirical studies have been done on the effect of BTA on bronze sculpture, none studied the corrosion protection of the film in an outdoor environment. [23,24] Hence a standard method of treatment used in the field of objects conservation does not exist. Within this project, BTA was evaluated for its performance as a corrosion inhibitor on outdoor bronze. BTA films were again tested for their protective affectivity on rolled bronze. The bronze samples were immersed in various BTA solutions for 1, 10, 100, or 1,000 minutes. Each sample was tested using 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 low frequency impedance modulus/electrical resistance, implying it provides a barrier to or inhibits the corrosion of the bronze.

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 that would dissolve in ethanol was 10.5%.

The samples were monitored using EIS during immersion. An application of an alternating current of 5 mV 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 cm^2 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. 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 graph. This concentration also left discoloration and crystalline patches on the surface of the bronze, after immersion, and therefore can not be recommended for use.

Figure 6, below, is a Bode plot of the initial BTA values, including the bare bronze. This plot shows how the BTA protects at various frequencies. 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-adsorbed 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 immersion 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.

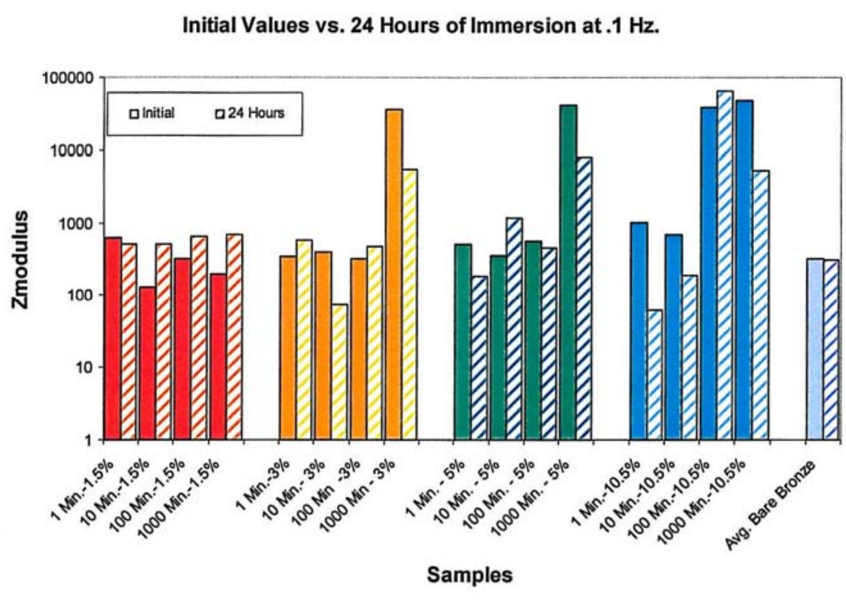

Figure 5. $|Z_{0.01\ Hz}|$ for various BTA Treated Samples

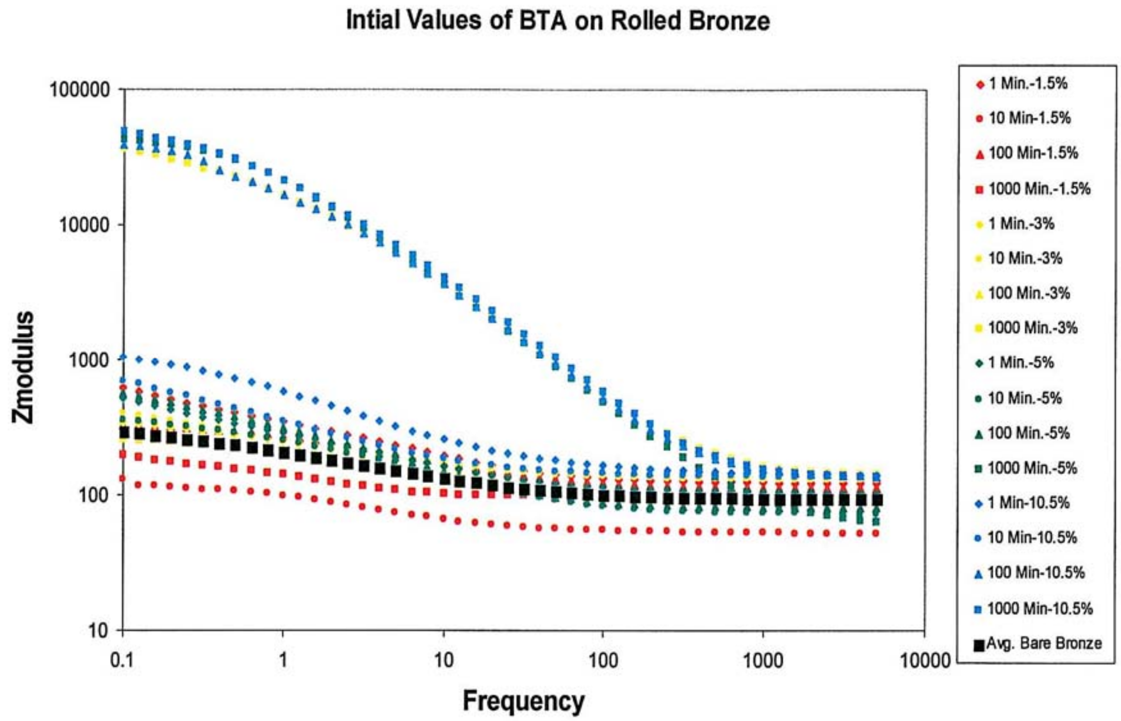

Figure 6. Bode Plots for Initial Protection of Bronzes By Various BTA Treatments

POSSIBLE USE OF *IN SITU* CORROSION SENSORS

Currently sensor development is underway at NDSU to monitor the coating protection *in situ*.[29] This technology would be a valuable tool for conservators to be able to monitor the condition of the coating on a scheduled basis. Bronze sculpture meets several of the requirements for use of dedicated *in situ* corrosion sensors. They have high value, they have a very long period of intended use, they are continually exposed to the environment, and they have a very high maintenance costs involved. Further, they are areas of high corrosion rate and potential areas on a sculpture where there is low visibility (i.e. the top of a sculpture) which would benefit greatly from the use of sensors. The work done at NDSU to date has focused on monitoring the corrosion protection of aircraft coatings. In summary, we have found that electrochemical noise methods for monitoring the electrochemical properties of coatings over metal substrates can be modified to use for *in situ* sensing of corrosion protection.[30] Figure 7, summarizing some of the recent results of this study, is shown. In this figure, the upper curve is the noise resistance, R_n, of the sample, the middle curve is the temperature in the cyclic exposure chamber, and the bottom curve is the localization index, and measure of the pitting tendency of the system, all plotted vs. the exposure time in the Prohesion Test chamber. It is intended that similar studies will be used on our bronze coatings.

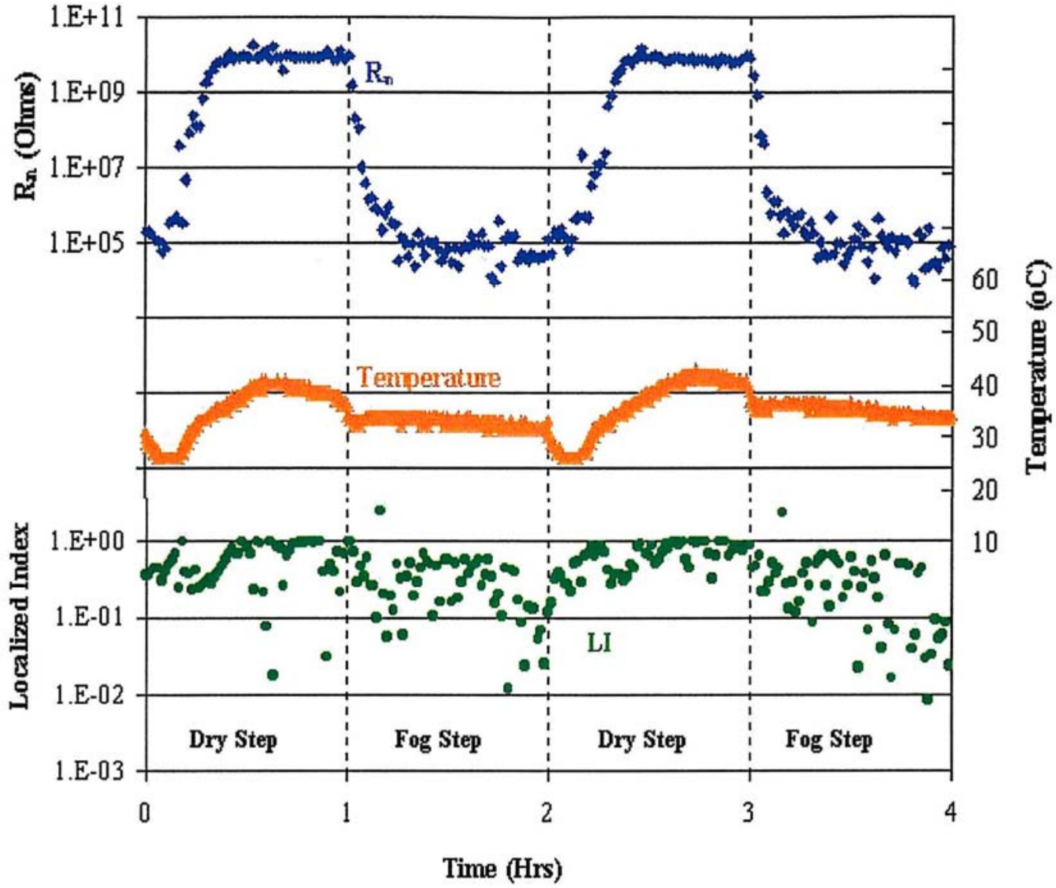

Figure 8. R_n, Temperature, and Localized Index vs. Time during 2 Prohesion cycles Measured in Exposure Chamber For Coatings over Al 2024 T-3

SUMMARY AND CONCLUSIONS

The presently used coatings for outdoor bronze protection have several deficiencies, and results were presented on initial studies to eliminate these insufficiencies. Our studies address the improvement of barrier and UV protection properties of bronze coatings by improved polymers, initially fluoropolymers, and by enhanced UV protection. The use of electrochemical methods to monitor the corrosion protection of such systems has proven useful and is a regularly used method of this study. Initial results are given. Further, a brief discussion of the possibility of the use of *in situ* sensors for monitoring the protection of the bronze by coatings is presented.

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