Materials Research Series

2001-09

Final Report to the
National Center for Preservation Technology and Training

Environmental Effects of Outdoor Pollutants on Cultural Resources:

Development and Testing of Organic Coatings for the Protection of Outdoor Bronze Sculpture for Air-Pollutant Enhanced Corrosion – Year 1

North Dakota State University
Fargo, ND 58105

Principle project contact: Prof. Gordon P. Bierwagen, Chair – Polymers & Coatings

Principal Investigator: Prof. Bierwagen

Research Assistant: Lisa Ellingson, Graduate Research Assistant

Research Assistance: Tara Shedlosky

Subcontractor Principal Investigator: Dr. E. Rene. De la Rie, Head Scientific Research

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NORTH DAKOTA STATE UNIVERSITY

FINAL REPORT
TO THE
NATIONAL CENTER FOR PRESERVATION TECHNOLOGY AND TRAINING
1999 GRANT PROGRAM

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

2. Project title: Development and Testing of Organic Coatings for the Protection of Outdoor Bronze Sculpture from Air-Pollutant Enhanced Corrosion —Year 1

3. Recipient: North Dakota State University Fargo, ND 58105

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ADMINISTRATIVE SUMMARY

1. Institution: North Dakota State University
Fargo, ND 58105

2. Project Title: Development and Testing of Organic Coatings for the Protection of Outdoor Bronze Sculpture from Air-Pollutant Enhanced Corrosion – Year 1

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

4. The proposed work is being performed at a rate reasonably close to schedule but we are asking for a 90 day no cost extension of the project to allow for delays in billing of the sub-contract to the National Gallery of Art.

5. Product of this research:
   a. We have submitted the Interim Report on the Project in March 2000.
   b. This Report contains the Administrative and Executive Summaries.
   c. The written Protocol is Appendix B of this Report.
   d. This is the Final Report of Phase 1.
   e. We have included on a CD in this package several POWERPOINT files from our work which include pictures of equipment and figures from the technical reports and presentations made from this work, as well as pictures of the personnel performing the work.

6. The projected and actual costs are quite close except for the following:
   a. The NGA is late in billing us for sub-contracting costs.
   b. The PI Salary needs were reduced because of an administrative promotion to Department Chair and some other salary expenditures appropriate to the contract were increased as well as material costs for new 85-5-5-5 (Cu-Pb-Zn-Sb) bronze test samples. The extra salary funds in our budget will be used for the costs of these new bronze samples which are to be used in Phase II of this program.

7. Attached is a copy of the budget breakdown and the remaining salary funds at our site that will be spent on the bronze samples.

8. The differences are discussed in item 6. above

9. The work on this grant has provided a test protocol for examining corrosion protective organic coatings on historic bronze artifacts, has expanded the use of quantitative, electrochemical characterization and evaluation of such coatings, and is beginning efforts towards developing improved coating materials for such artifacts.

10. Some of this work has been presented (see above in technical report). We intend to publish this work in several venues- professional journals pertinent to the fields of Conservation, Organic Coatings and Electrochemistry. Part of this work will be reported at METAL 2001 in April 2001 in Santiago Chile, and we intend to submit part of the work to EIS 2001, the 5th Annual International Symposium on Electrochemical Impedance Spectroscopy in Marilleva, Italy, June 2001.

11. The Test Protocol for the Characterization of Corrosion Protective Properties on Coatings over Bronzes is submitted with this report.

Summary of Fund #4085 NCPTT Grant #MT-2210-9-NC-20					
P.I. G. Bierwagen - US Dept. of Interior-Development and Testing...Bronze Sculture...					
Salary Commitments: Ellingson, Shedlosky, Bierwagen, Johnson					
Category: Budget category					
#	**Catagory**	**Beginning Balance**	**Balance**	**Category Balance**	**Cumulative Expenses**
1	Salaries	$20,690.00	$3,876.17		$16,813.83
3	Fringe	2,031.00	1,251.30	5,127.47	779.70
4	Travel	3,667.00	379.63		3,287.37
5	Supplies	1,620.00	(5,507.10)	(5,127.47)	7,127.10
6	Contractual	10,000.00	10,000.00	10,000.00	0.00
	Total:	**$38,008.00**	**$10,000.00**	**$10,000.00**	**$28,008.00**

Total beginning balance as of 9-1-99: $38,008.00

***Effective Date: 09-01 -99 Termination Date: 09-30-00**

Institution: North Dakota State University Fargo, ND 58105

Project Title: Development and Testing of Organic Coatings for the Protection of Outdoor Bronze Sculpture from Air-Pollutant Enhanced Corrosion - Year 1

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

Executive Summary

The goal of this research throughout the first year was to use electrochemical methods to examine previously coated samples that were weathered in the research project at the National Gallery of Art. The performances of five coating systems on satin-finish, cast monumental bronze substrates were studied using electrochemical impedance spectroscopy. All five coatings underwent accelerated weathering in a Prohesion® and QUV® cabinet in accordance with ASTM D 5894-96 "*Standard Practice for Cyclic Salt Fog/UV Exposure of Painted Metal (Alternating Exposures in a Fog/Dry Cabinet and a U V/Condensation Cabinet)* ". To date, all five coating systems were removed from accelerated weathering exposure after visible failure. Electrochemical impedance spectroscopy data was used in determining failure of the coating systems and ranged from accelerated exposure times of 14 252 days. Rankings of the five coating systems were determined as: BTA pretreatment + BASF Acrylic Urethane + wax > Nikolas 11565 Acrylic + Nikolas 9778 Acrylic Urethane + wax>> Incralac + wax > Waterborne Acrylic Urethane + wax> BTA pretreatment + wax > bare bronze.

Introduction

This research addresses the increasing 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 corrodents such as SO_x, NO_x, CO_2, and chlorides. These corrodents affect various materials located outdoors and monumental bronze is no exception. 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 effect the severity of atmospheric corrosion that include: temperature, corrosion products, passive film formation, electrolyte thickeness, and metal composition.[1] The location of bronze sculpture in high pollution urban areas is potentially very harmful and reduces their longevity.

Protection from bronze corrosion is thus very important when trying to conserve the bronze sculpture situated in a 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 protective of the bronze to inhibit corrosion from occurring.

Minimizing the corrosion of bronze can be done by using coatings on the monuments.. Coatings provide a barrier between the corrodents 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 solvable with toluene, while the wax is also considered removable. 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 it's 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 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.

Methods and Materials

The polished, monumental bronze samples were received from the National Gallery of Art, Washington D.C. Complete details of sample preparation and descriptions of samples can be found in the 1997 Final Report by NGA entitled" Research into Protective Coating Systems for Outdoor Bronze Sculpture and Ornamentation. Phase II" page 5.[4] A brief description of the samples will be given within this report.

A total of six satin-finished, cast monumental bronze panels were received by North Dakota State University for electrochemical impedance spectroscopy analysis. Coating systems on these samples were 1) Incralac® + wax, 2) Benzotriazole pretreatment + wax, 3) Nikolas acrylic urethane + acrylic urethane + wax, 4) Benzotriazole pretreatment + BASF acrylic urethane + wax, 5) Nikolas waterborne acrylic urethane + wax, and 6) bare, monumental bronze. Initial pictures, or pre-accelerated exposure pictures, can be found in Figures 1-6.

Accelerated Weathering

Samples underwent cyclic exposure in a Prohesion® and QUV® chamber (Figure 7) in accordance with ASTM D 5894-96 "*Standard Practice for Cyclic Salt Fog/U V Exposure of Painted Metal, (Alternating Exposure in a Fog/Dry Cabinet and a U V/Condensation Cabinet)*". Samples in the Prohesion® chamber were exposed to an environment that cycles between one hour of salt fog at 25°C and one hour of no fog at 35°C. The salt fog used for weathering was dilute Harrison solution (0.35 wt. % $(NH_4)_2SO_4$ and 0.05 wt. % NaCl in H_2O). Exposure in the QUV® cabinet consisted of four hours of exposure to 340 nm UV-A at 60°C, alternated with 4 hours of condensation at 50°C.

This method allowed for a controlled environment where corrosion was accelerated. No exposure is truly an accurate representation of real world conditions, but this method did provide an environment that was capable of providing samples to corrode at a faster rate and thus rank the coatings more rapidly.[5]

Electrochemical Impedance Spectroscopy

Electrochemical methods such as electrochemical impedance spectroscopy are techniques that provide a quantitative analysis of a corroding material.[6] The impedance of protective coatings is determined by application of a small, sinusoidal current (1-10 mV generally) to the electrochemical cell. An ideal circuit for a protective coating system over a metal substrate is displayed in Figure 8. This circuit incorporates both capacative and resistive properties to the coating system. The electrolyte solution, dilute Harrison solution, is presumed to consist of resistive properties, denoted as R_s in the circuit. The coating system circuit consists of C_{ct}, the charge transfer capacitance, R_p represents the pore resistance, and finally C_{dl} denotes the double layer capacitance. These circuit elements aid in understanding the corrosion behavior of the coating system[7]

Electrochemical impedance spectroscopy (EIS) is one such electrochemical method that can be utilized to characterize the corrosion protection of coatings.[8,9,10,11,12,13] 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.[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.

Results and Discussion

All EIS data was analyzed using Bode plots (log impedance verses log frequency) and are shown in Figures 10 – 17. Initially the impedance of the bare bronze sample at the low frequency of 0.1 Hz was 368.135 $\mathbf{\Omega}$ as shown in Figure 10. After 8 days of exposure in the QUV® cabinet the impedance fell to 157.803 $\mathbf{\Omega}$. Lack of an oxide layer to provide less corrosion protection. Visual assessment alone after 8 days denoted a large amount of corrosion occurring due to coverage of green corrosion products on the substrate. Pictures of the bare bronze before and after exposure are shown in Figure 6.

The initial impedance value of 368.135 $\mathbf{\Omega}$ for the uncoated bronze sample implies that any higher value would indicate some form of increased corrosion resistance. Oxide layer formation or the coating system providing a barrier to electrolyte and ion transfer are two examples of why this increased resistance may occur. Benzotriazole pretreatment + wax on the bronze substrate initially showed a slightly higher impedance value than the bare bronze (3.40 x 10^3 $\mathbf{\Omega}$), although it is noted that this impedance value is still very low and thus provides minimal corrosion protection. Figure 11 shows that after one day of QUV® exposure, the impedance increased to 4.53×10^4 **Ω**. This increase in impedance may be due to an increased oxide formation thus allowing corrosion protection. This increased impedance quickly diminished after 14 days of exposure when the impedance dropped to 296.294 **Ω**. Remembering that the impedance of the uncoated bronze was 368.135 **Ω**, this value of 296.294 **Ω** demonstrated that the benzotriazole + wax coating was providing no corrosion protection. Visual assessment of the benzotriazole + wax sample clearly showed a lack of corrosion protection after 14 days of exposure (see Figure 2).

A common coating system for bronzes currently in use today within the United States, Incralac® + wax, initially showed very good corrosion resistance (3.86×10^8 **Ω**). The bode plot for this sample is shown in Figure 12. Decreased impedance was noted after 14 days of exposure and this decrease continued until failure was determined ($Z = 1.35 \times 10^4$ **Ω**) after 140 days of exposure. Although 1.35×10^4 **Ω** impedance is not exactly the impedance that was determined for the bare bronze sample, it is still approximately 10^4 **Ω**, which indicates a very poor corrosion protection coating.

The third coating over monumental bronze analyzed by impedance spectroscopy was Nikolas 11565 acrylic + Nikolas 9778 acrylic urethane + wax system. This coating displayed very high impedance initially of 8.28×10^8 **Ω**. This high impedance (> 10^6 **Ω**) was maintained by this coating system for over 210 days in accelerated exposure conditions as shown in Figure 13. The long duration of high impedance by the acrylic urethane suggested good overall corrosion protection of the monumental bronze, especially when compared to the Incralac® + wax system. This sample was finally removed from accelerated exposure testing after 252 days when the impedance was 8.28×10^4 **Ω**. Overall this coating showed great promise as a potential replacement for the Incralac® + wax system.

The fourth bronze sample, BTA pretreatment + BASF 923-85 acrylic urethane + wax, behaved similarly to the third coating system by maintaining high impedance over a long duration of accelerated exposure. Initially an impedance of 1.50×10^8 **Ω** was reported. A slow decrease in impedance from 10^9 to 10^6 **Ω** occurred after 168 days of exposure (see Figure 14). An impedance of 10^6 **Ω** was maintained for 70 more days until at 252 days of accelerated exposure impedance of 1.19×10^5 **Ω** was observed and the sample was removed from exposure. This coating again showed similar behavior to the other acrylic urethane coating (#3) and may also be a possible replacement coating for the Incralac + wax system.

The final coating system studied was the waterborne acrylic urethane. This coating did not show much promise as shown in the EIS data in Figure 15. Initially it provided good corrosion protection with impedance of 2.18×10^8 **Ω**, but after only 56 days of exposure the value fell to 3.37×10^3 **Ω**. Overall this coating corroded very quickly as compared to the other urethane coating systems and is thus considered an inadequate replacement for a corrosion protection coating for outdoor bronze.

Conclusion

Electrochemical impedance spectroscopy combined with accelerated exposure testing allowed for the failure rate of five coating systems over satin-finished, cast monumental bronze to be determined. All coatings were compared to the current coating in use throughout the United States, Incralac® + wax, to assess if any potential replacements was possible. Overall the rankings of the coatings were: BTA pretreatment + BASF Acrylic Urethane + wax > Nikolas 11565 Acrylic + Nikolas 9778 Acrylic Urethane + wax>> Incralac + wax> Waterborne Acrylic Urethane + wax> BTA pretreatment + wax> bare bronze. Both acrylic urethane solvent borne systems showed increased corrosion protection of the monumental bronze. Failure of the Incralac® + wax sample occurred after only 140 days of accelerated exposure, while both acrylic urethanes provided corrosion protection through 252 days. These two coatings show promise as potential replacements of Incralac® + wax.

Presentations:

"Evaluation of Various Coating Systems on Bronze Using EIS and Accelerated Test Methods," with Lisa Ellingson, Gordon Bierwagen, Lynn Brostoff, B. Rene de la Rie, & Tara Shedlosky, presented as a poster in Symposium Z1, 197th Meeting of the Electrochemical Society, Toronto, Canada, May 2000.

"Evaluation of Various Coating Systems on Bronze Using EIS and Accelerated Test Methods," with Lisa Ellingson, Gordon Bierwagen, Lynn Brostoff, E. Rene de la Rie, & Tara Shedlosky presented as a poster in the 28th American Institute for Conservation of Historic & Artistic Works Annual Meeting, Philadelphia, June 2000.

"The Application of Digital Image Analysis to the Performance Assessment of Coatings on Bronze and Copper Samples," Tara Shedlosky & Lynn Brostoff presented as an oral presentation in the 28th American Institute for Conservation of Historic & Artistic Works Annual Meeting, Philadelphia, June 2000.

"Electrochemical Investigation of Corrosion Protective Coatings for Historical & Architectural Artifacts", Gordon Bierwagen, Invited Lecture, Andrew Mellon Visiting Lecturer Series, National Gallery of Art, June 19, 2000.

Acknowledgments

This work was made possible by funding from the National Center for Preservation Technology and Training fund **MT-2210-9-NC-20.** All bronze sample preparation and coating applications were performed at the National Gallery of Art in Washington D.C.

References

[1] Tullmin, M. a. P. R. R. (2000). Atmospheric Corrosion. Uhlig's Corrosion Handbook. R. W. Revie, John Wiley & Sons, Inc.: 305-321.
[2] Naude, V. N., and Glenn Wharton (1995). Guide to the Maintenance of Outdoor Sculpture. Washington D.C., American Institute for Conservation of Historic and Artistic Works.
[3] Weil, P. D. (1980). The Conservation of Outdoor Bronze Sculpture: A Review of Modem Theory and Practice. AIC Preprints, San Francisco, The American Institute for Conservation of Historic and Artistic Works.
[4] See L.Brostoff and E.Rene de la Rie, "Final Report to the NCPTT 1997 Grant Program: Research into Protective Coating Systems for Outdoor Bronze Sculpture and Ornamentation. Phase II" or L.Brostoff and E.Rene de la Rie, "Final Report to the NCPTT 1998 Grant Program: Research into Protective Coating Systems for Outdoor Bronze Sculpture and Ornamentation. Phase III" for information containing sample preparation and product information.
[5] 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).".
[6] G.P.Bierwagen, C.Jeffcoat, D.J.Mills, J.Li, S.Balbyshev, D.E.Tallman, **Prog. Organic Coatings, 29** (1996) 21. A. Wain, J. Alverez and T.H. Randle, "Electrochemical Noise for Evaluation of Coatings on Museum Artifacts," *Ibid.*, paper 126, p. 669.
[7] Otieno-Alego, V. a., Graham Heath, David Hallam and Dudley Creagh (1998). Electrochemical Evaluation of the Anti-Corrosion Performance of Waxy Coatings for Outdoor Bronze Conservation. METAL 98, 1998 James & James (Science Publishers) Ltd.
[8] N. D. Cremer, *Prohesion Compared to Salt Spray and Outdoors: Cyclic Methods of Accelerated Corrosion Testing*, Presentation at Federation of Society for Coatings Technology 1989 Paint Show.
[9] D.A. Jones, *Principles and Prevention of Corrosion,* 2nd Ed., Prentice-Hall, Upper Saddle River, NJ, 1996.
[10] Skerry, B.S.;Eden, D.A.,"Electrochemical Testing to Assess Corrosion Protective Coatings", **Prog Organic Coatings, 15** (1987) 269-285.
[11] F. Mansfield, *Corrosion Science*, Vol. 40, No. 6, 1998, pp.1045.
[12] G.P.Bierwagen, "Reflections on Corrosion Control by Coatings," **Prog. Organic Coatings, 28** (1996) 42-48.
[13] Electrochemical Noise Measurement (ENM) is another commonly used electrochemical method. See: G.P.Bierwagen, *.J.Electrochem. Soc.* **1994**, L141.

Figure 1

Initial (day 0) and Failure (day 140) of Incralac + Wax

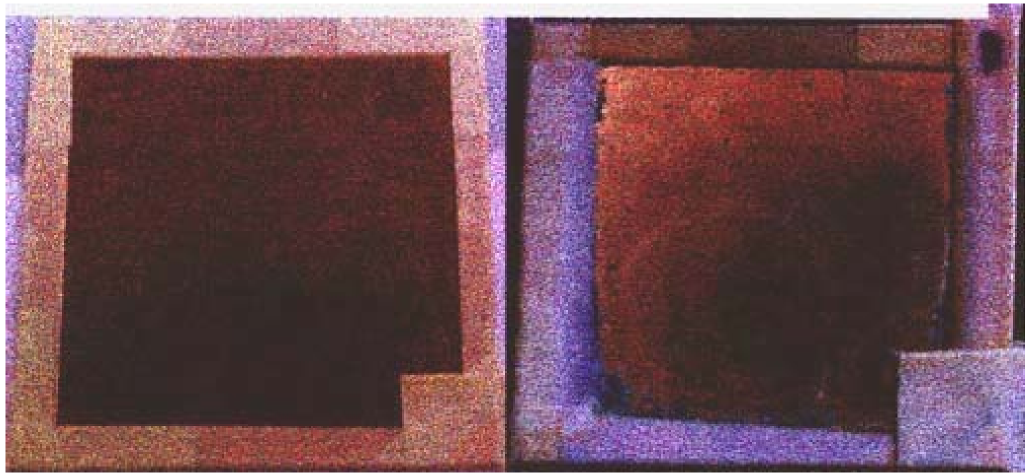


Figure 2

Initial (day 0) and Failure (day 14) of Benzotriazole Pretreatment + Wax

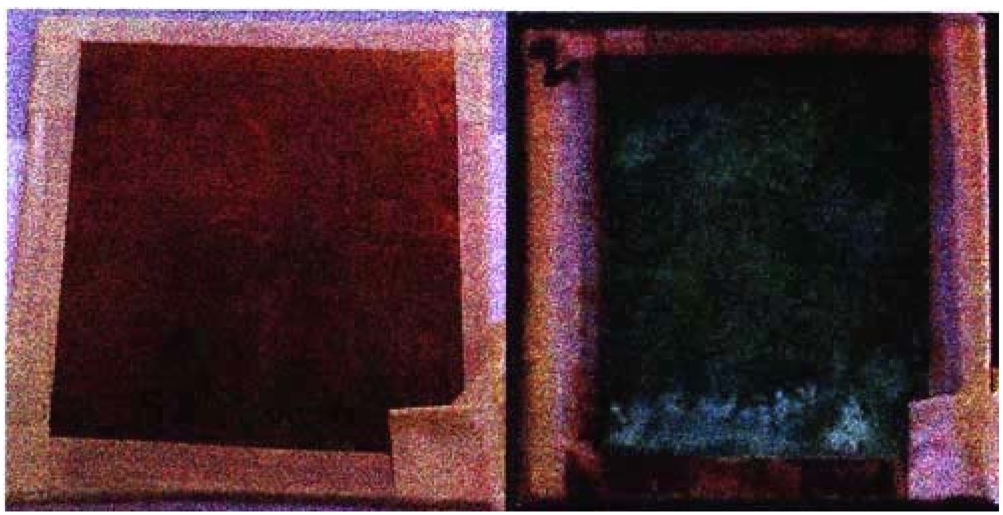


Figure 3

Initial (day 0) and Failure (day 252) of Nikolas Acrylic + Acrylic Urethane + Wax

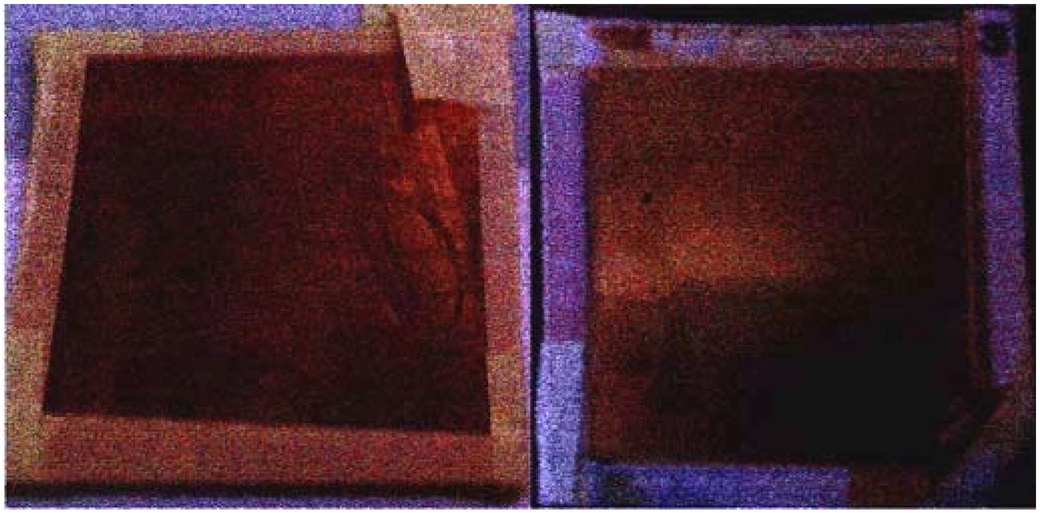


Figure 4

Initial (day 0) and Failure (day 252) of Benzotriazole Pretreatment + BASF Acrylic Urethane + Wax

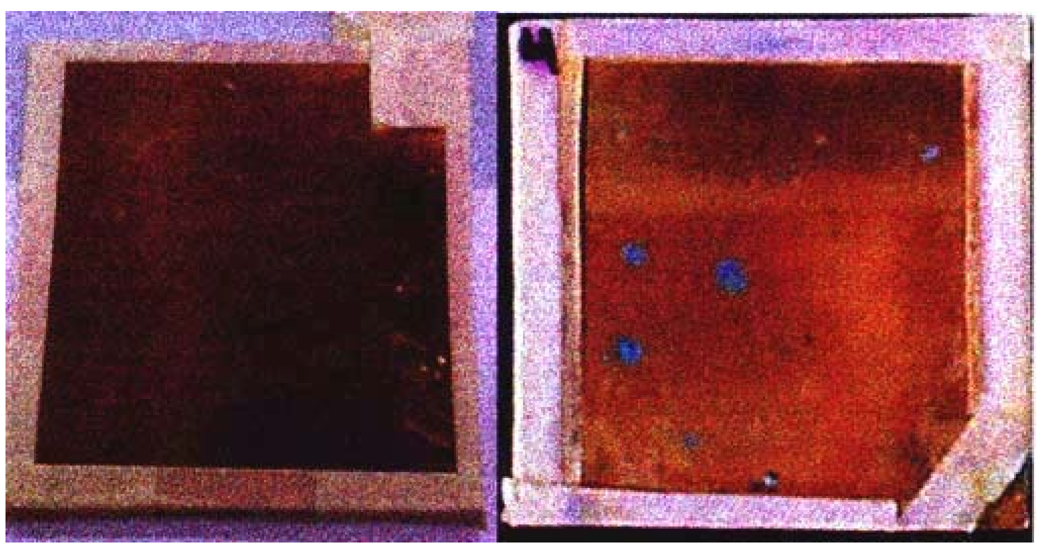


Figure 5

Initial (day 0) and Failure (day 56) of Nikolas WB Acrylic Urethane + Wax

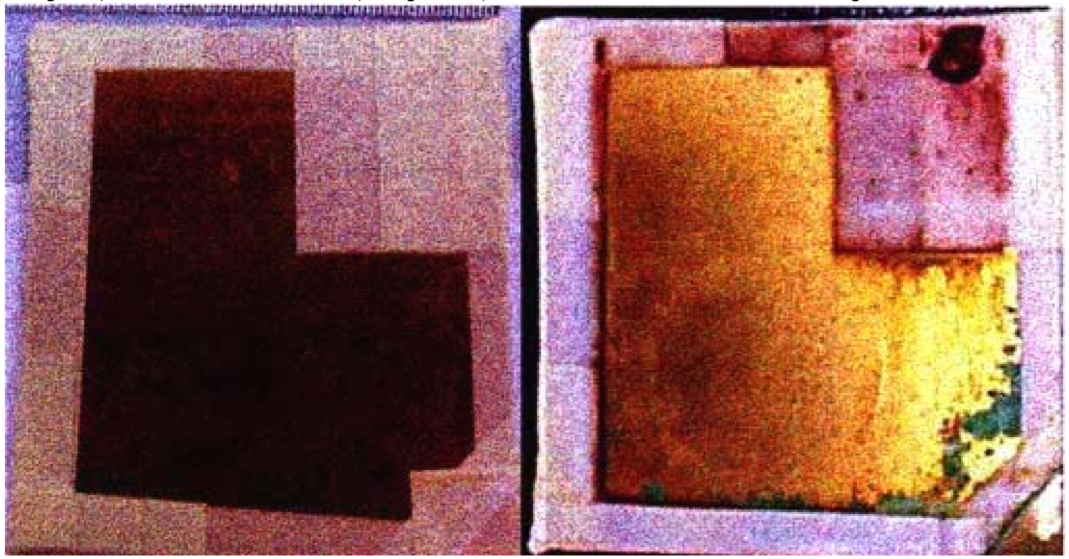


Figure 6

Initial (day 0) and Failure (day 18) of Bare Bronze

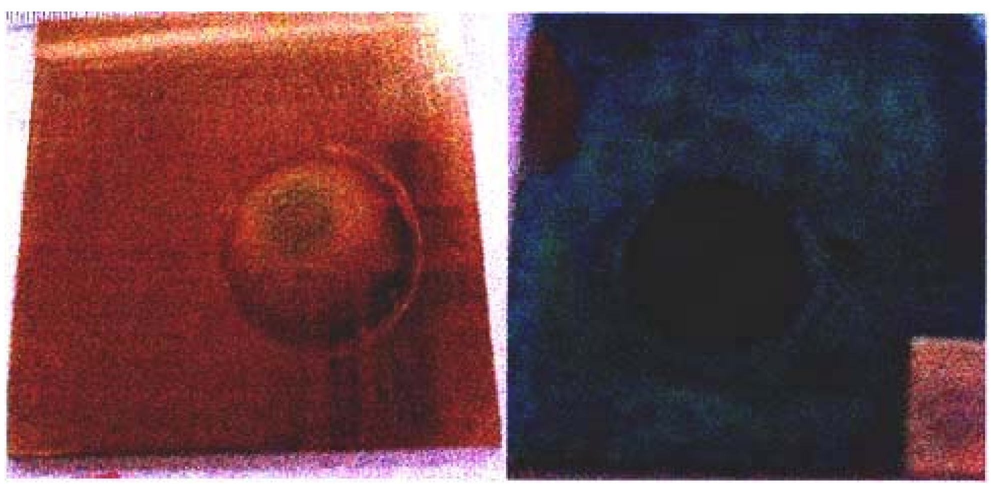


Figure 7

Prohesion® and QUV® Accelerated Exposure Cabinets

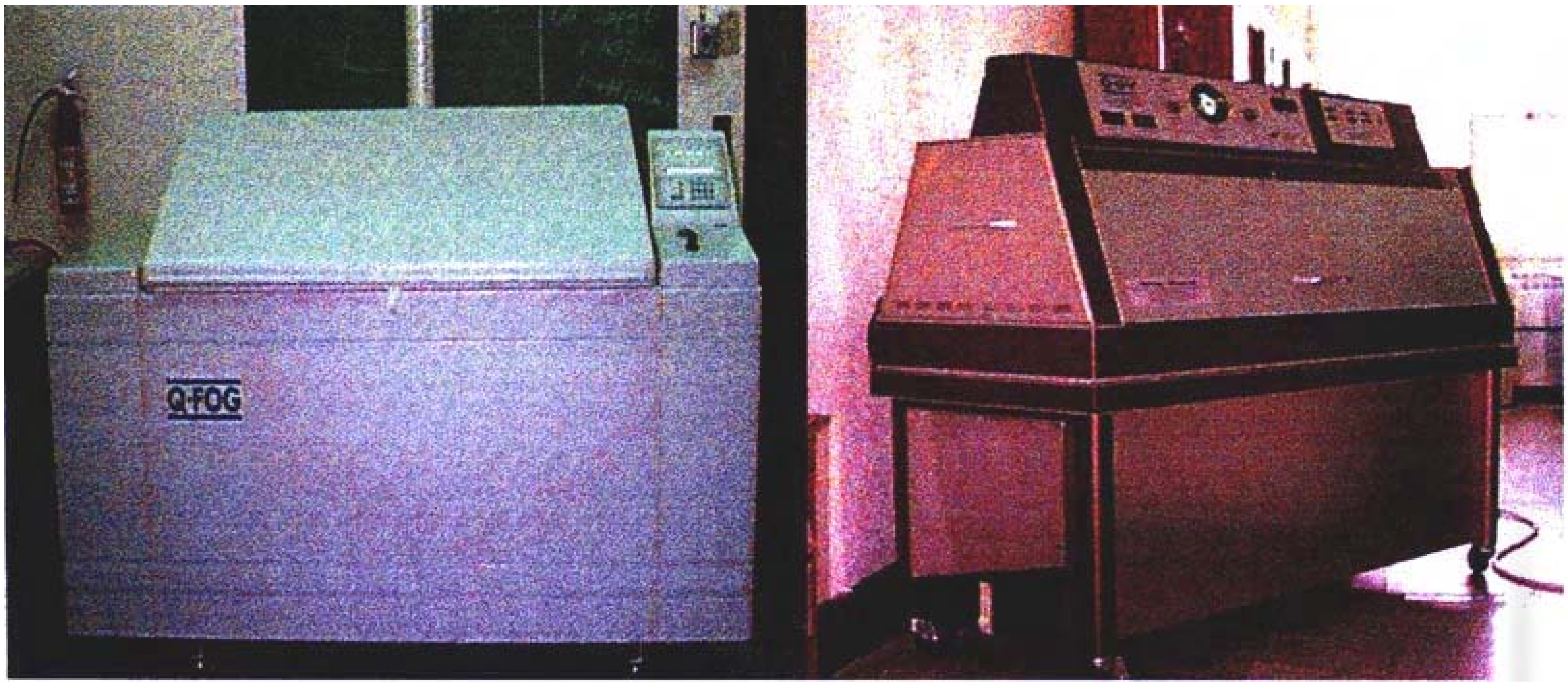
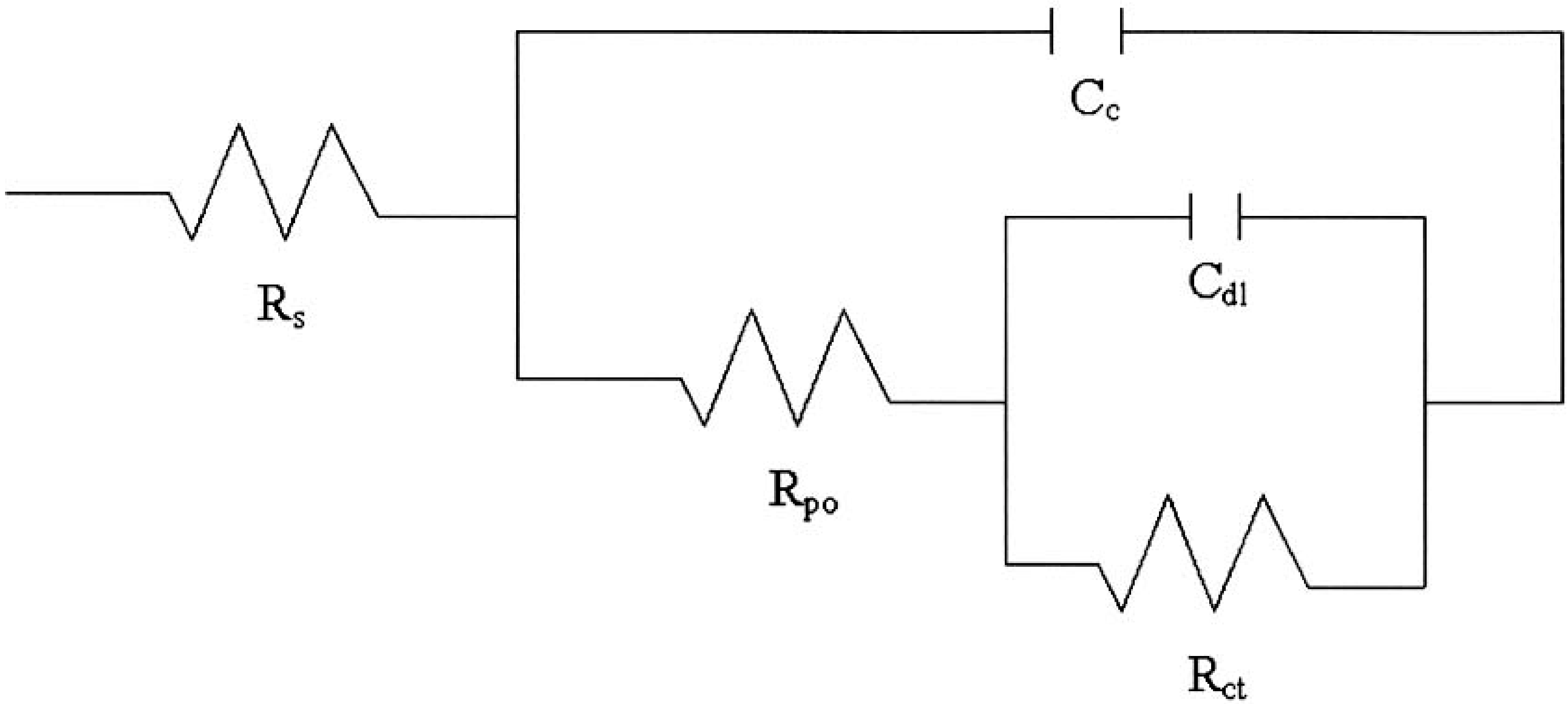


Figure 8

Circuit Representation of A Coated Metal



R_s = Solution resistance
C_c = coating capacitance
R_{po}= Pore resistance
R_{ct}= Charge transfer resistance
C_{dl}= Double layer capacitance

Figure 9

Picture of a Sample Setup for Electrochemical Impedance Spectroscopy

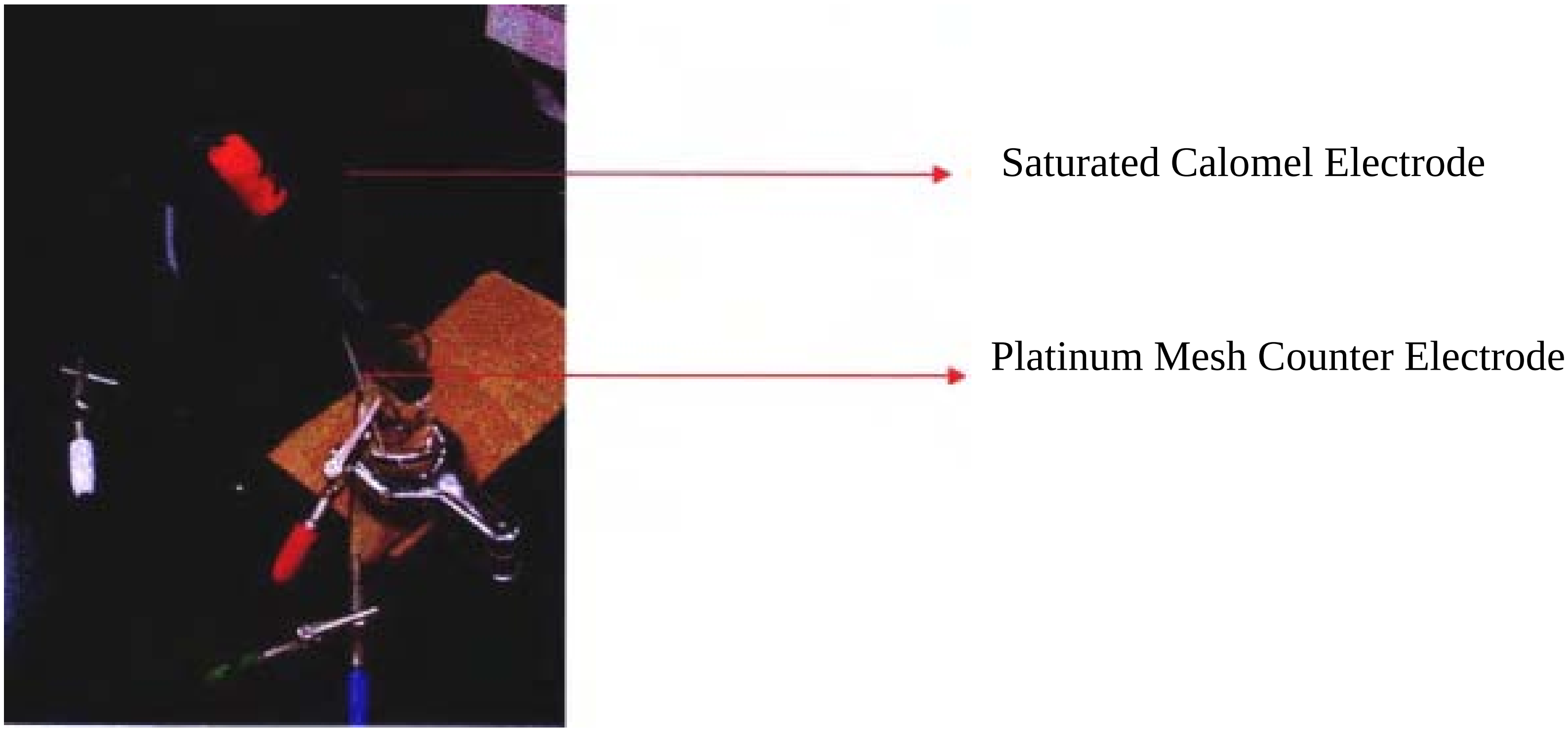


Figure 10

Bode Plot of Polished Bare Bronze Sample During Prohesion® and QUV® Cycling

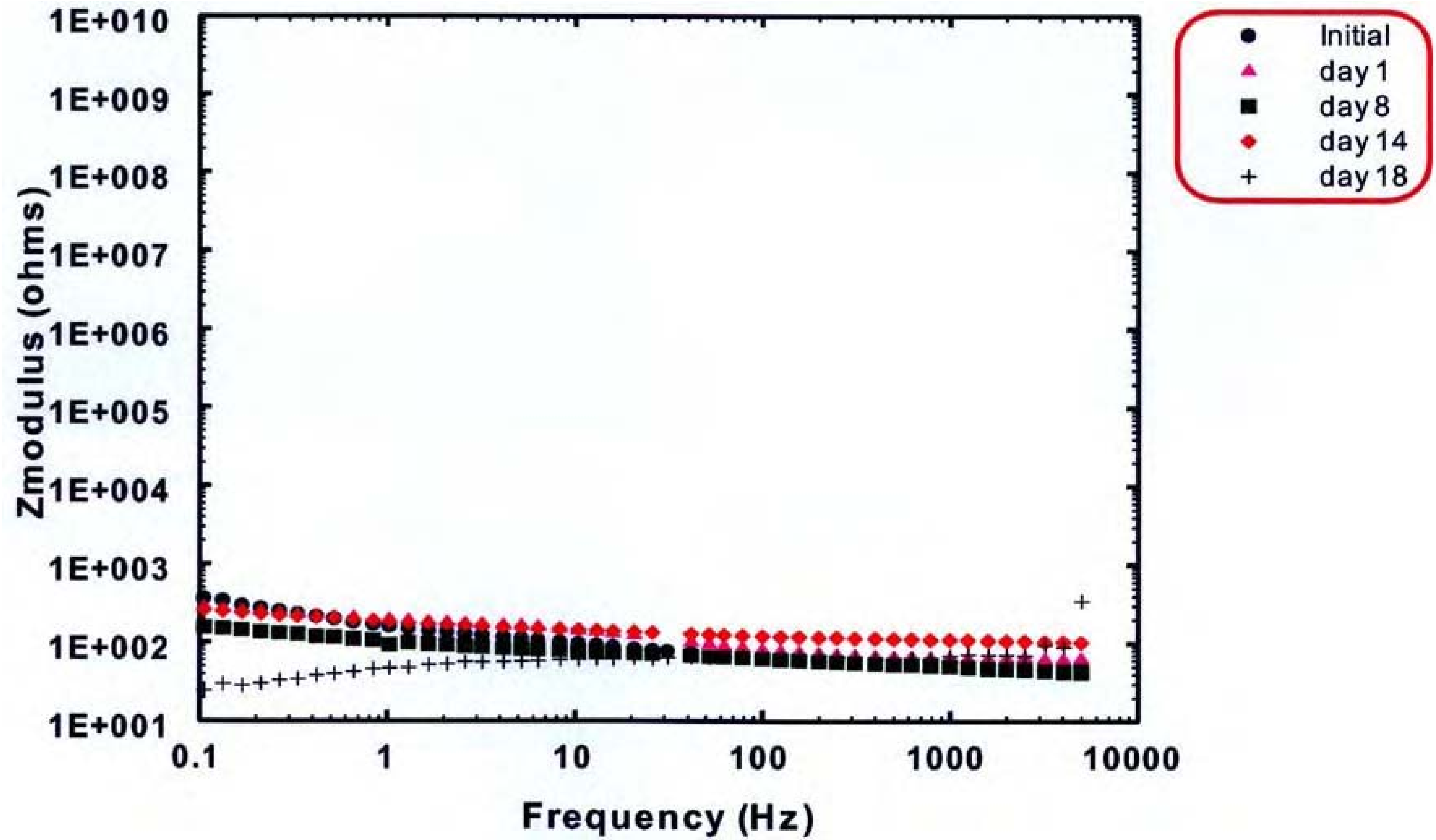


Figure 11

Bode Plot of Polished Bronze Sample with Incralac + Wax During Prohesion® and QUV® Cycling

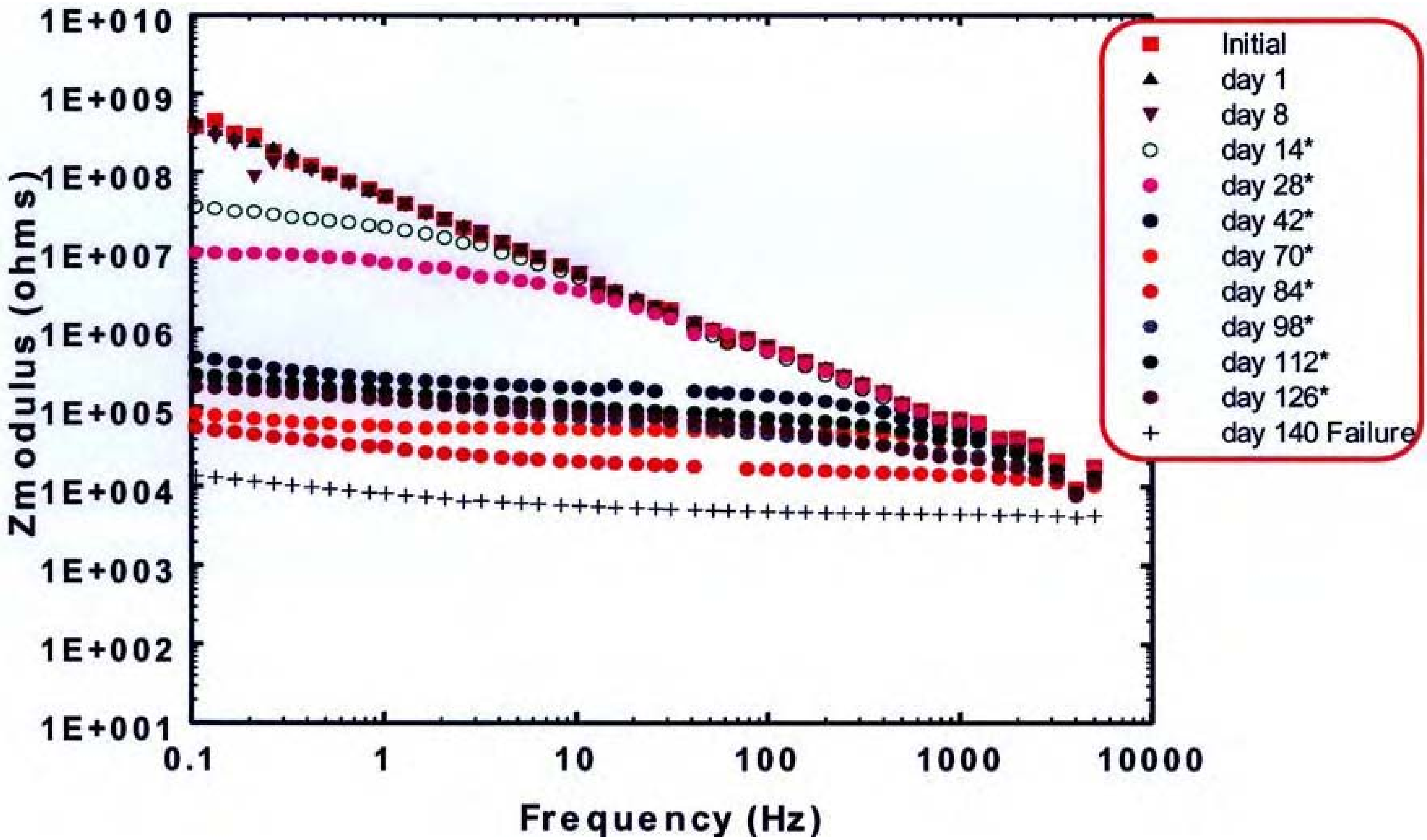


Figure 12

Bode Plot of Polished Bronze Sample with Benzotriazole Pretreatment + Wax During Prohesion® and QUV® Cycling

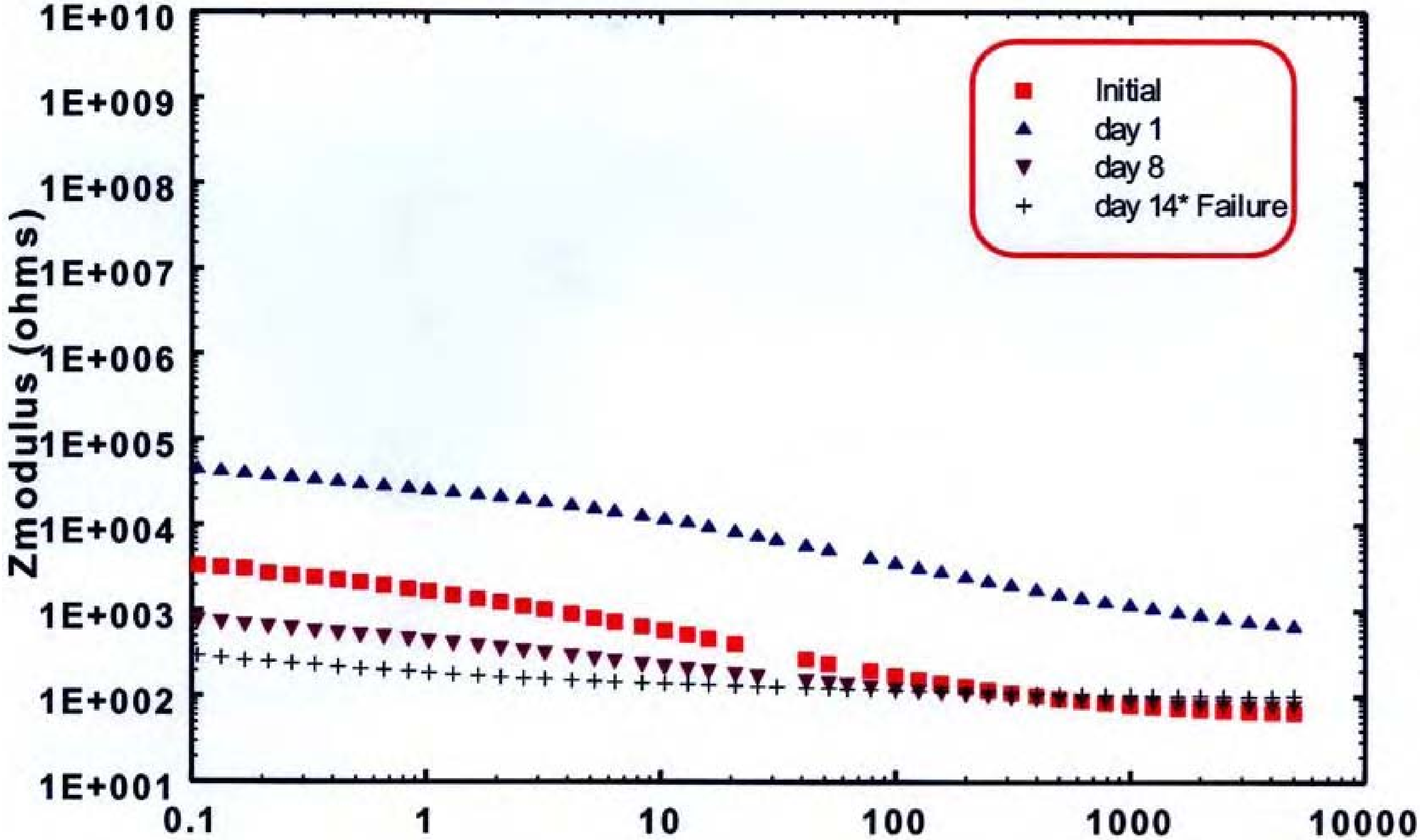


Figure 13

Bode Plot of Polished Bronze Sample with Nikolas Acrylic + Acrylic Urethane + Wax During Prohesion® and QUV® Cycling

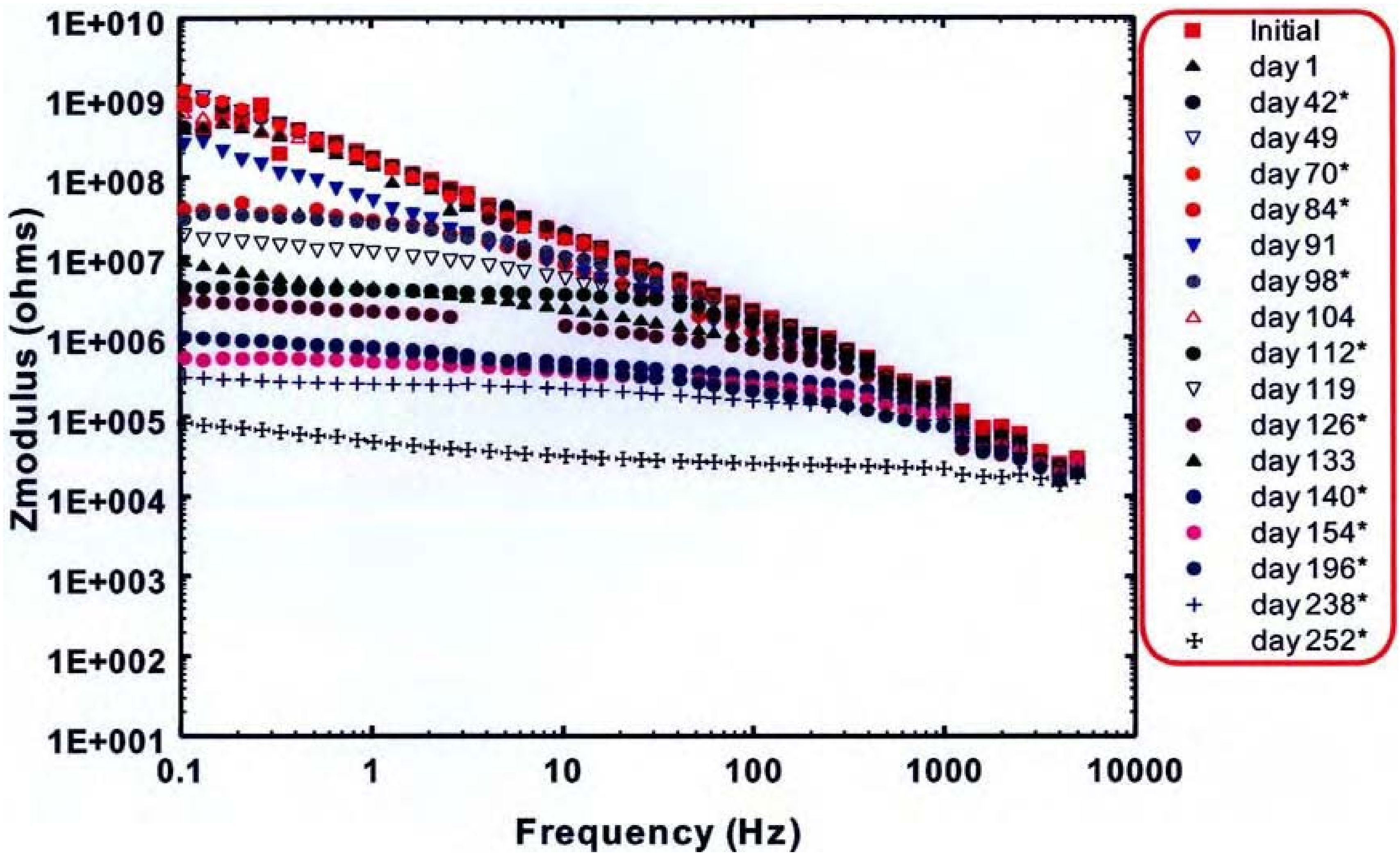


Figure 14

Bode Plot of Polished Bronze Sample with Benzotriazole Pretreatment + BASF Acrylic Urethane + Wax During Prohesion® and QUV® Cycling

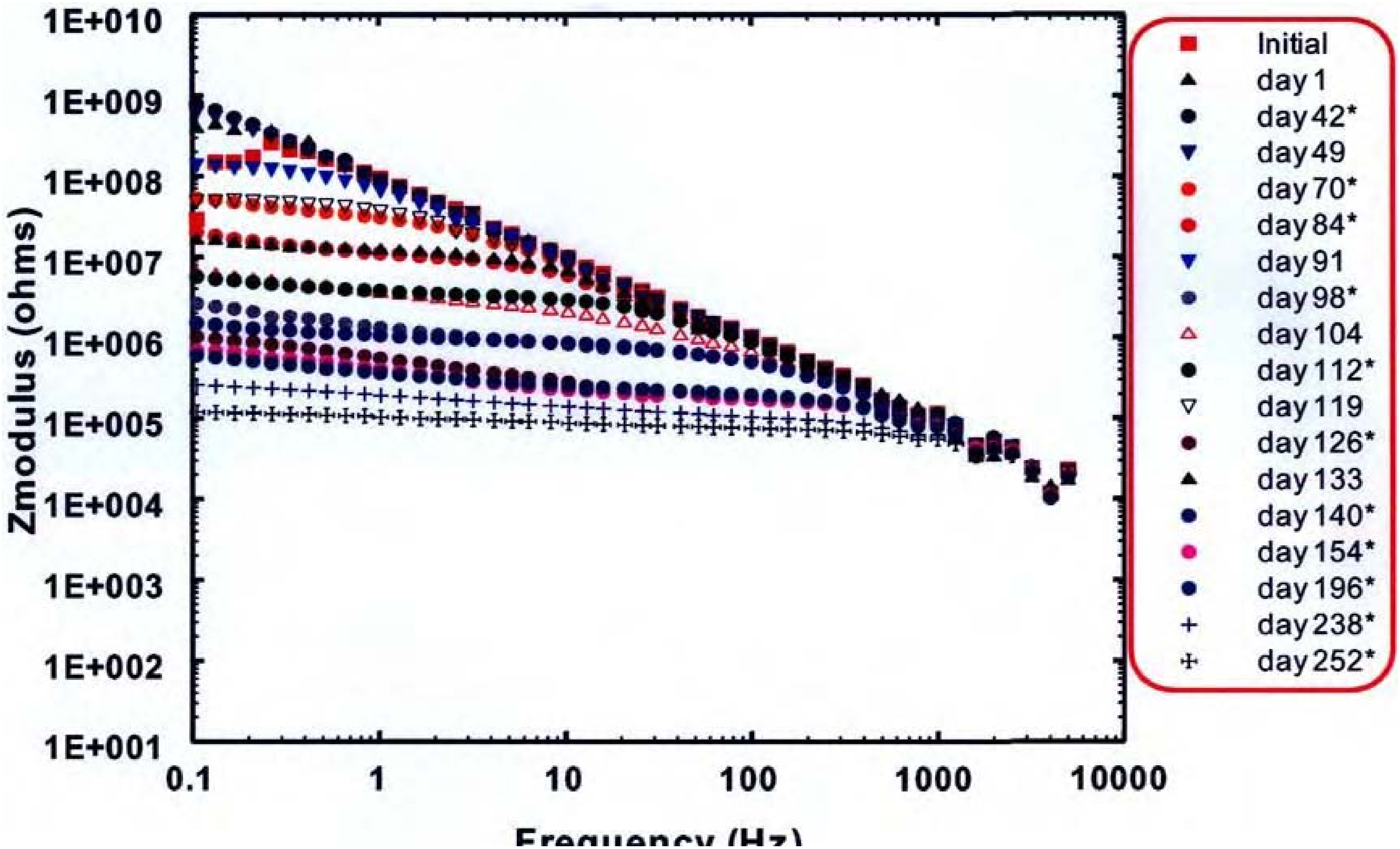


Figure 15

Bode Plot of Polished Bronze Sample with Nikolas WB Acrylic Urethane + Wax During Prohesion® and QUV® Cycling

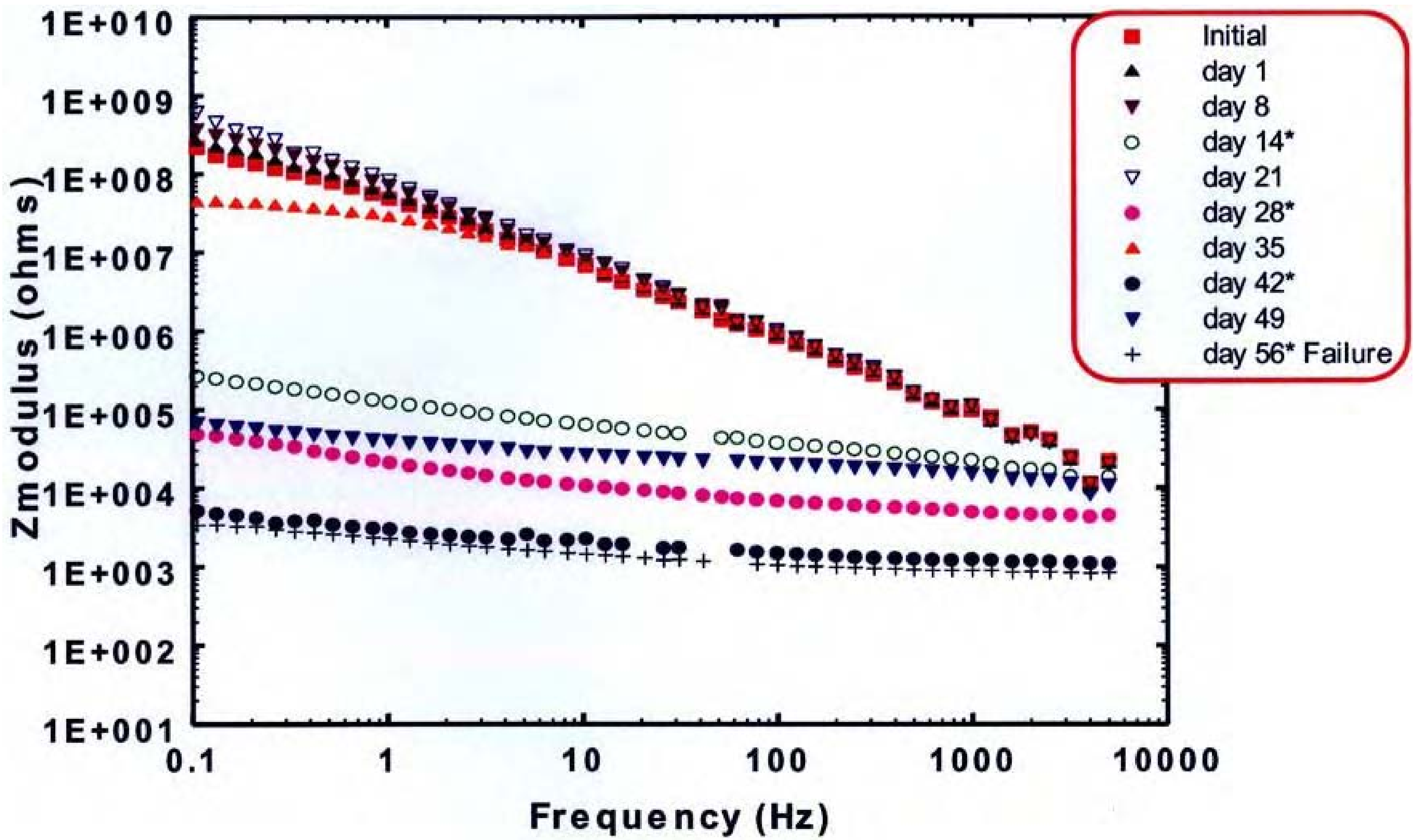


Figure 16

Bode Plots of Polished Bronze Samples
During Prohesion® and QUV® Cycling

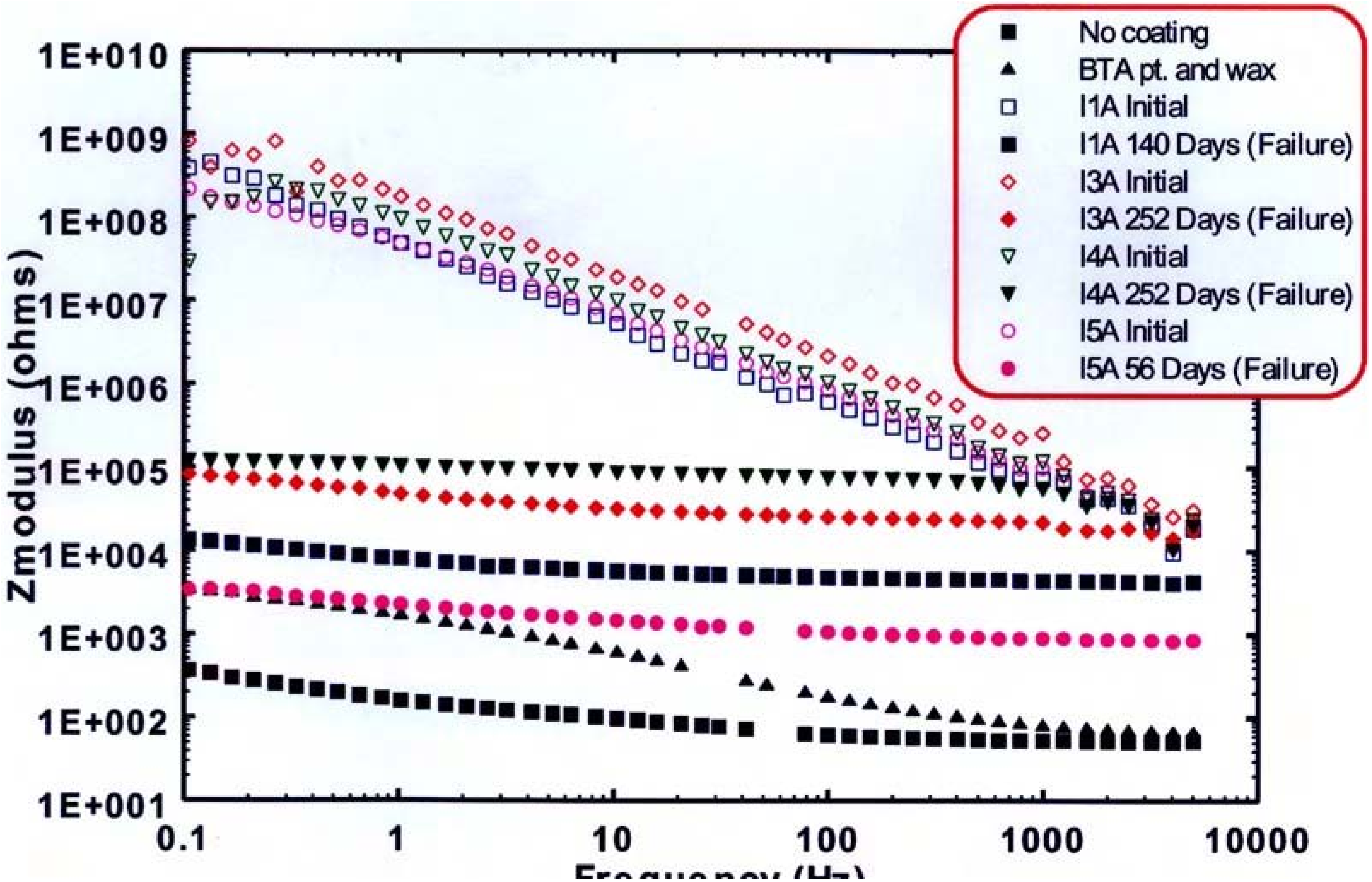
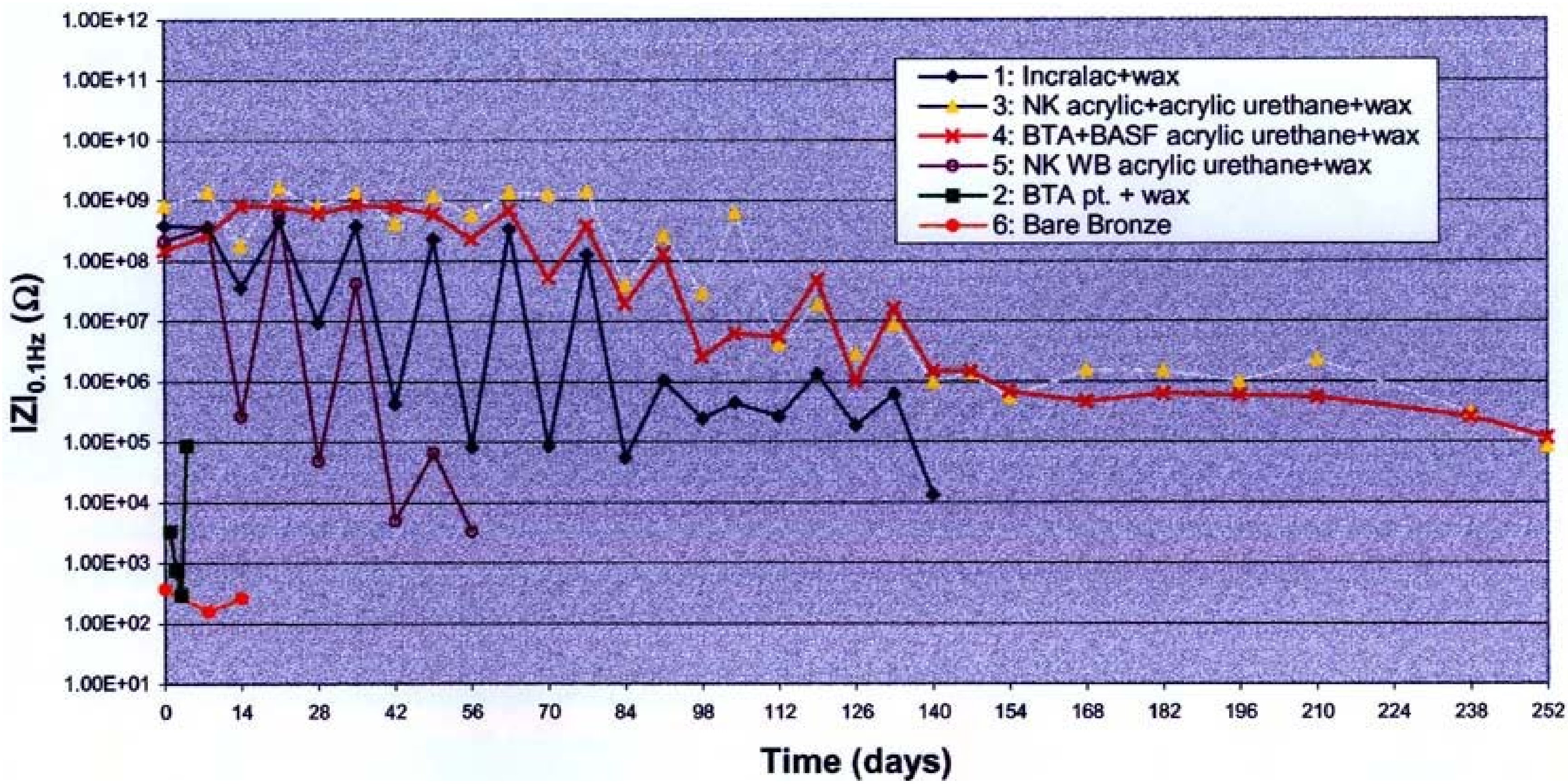


Figure 17

|Z| 0.1 Hz vs Time for NGA Samples Under QUV/Prohesion Exposure



Appendix A

The Weathering Effects of Benzotriazole (BTA) on Rolled Bronze

Tara J. Shedlosky*, Lisa Ellingson, Dr. Gordon Bierwagen
Department of Polymers and Coatings
North Dakota State University, Fargo, ND
* Research carried out while at the National Gallery of Art Washington, DC

Abstract

Benzotriazole (BTA) films were 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 artificially weathered and tested using electrochemical impedance spectroscopy (EIS) and digital imaging analysis. Overall results show that BTA provides only minimum protection against outdoor weathering, but under specific preparations does afford significant initial resistance.

Introduction

Benzotriazole (BTA) was first used as a restrainer in photographic emulsion and a reagent for the quantitative analysis of silver. It was then found to be an effective coating to prevent both atmospheric and underwater corrosion of copper.[14] 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 that forms when cuprous chloride is converted to cupric chloride.[15] BTA has been 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 as seen in Figure 1.

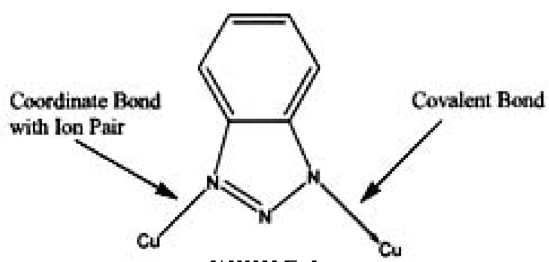


Figure 1

BTA can utilize the lone pairs on the Nitrogen to bond to the Copper ions. According to the literature the BTA appears to chemisorbe onto the copper oxide surface to form a Copper-B TA coordination polymer film.[16]

A recent study looked at Cu-BTA films using reflection-absorption infrared spectroscopy and found that the film thicknesses of the Cu-BTA generally increase linearly with time of immersion, and that the growth rate is dependent on both the concentration and the solvent.[17] The BTA thicknesses ranged from 100 to 400A. This research project's aim was to see if there is an ideal preparation of BTA to bronze for outdoor protection.

BTA has been used for years to stabilize objects that are housed inside, but BTA is also being applied on outdoor sculpture. Although there have been many empirical studies on the effect of BTA on bronze samples there has not been a study measuring the corrosion protection of the film in an outdoor environment. Hence a standard method of treatment used in the field of Objects Conservation does not exist. This research looked at the weathering effects when varying the concentration of the BTA, the solvents used to dissolve the BTA, and the time rolled bronze was immersed in the BTA solution.

Experimental

Lullaboy rolled spring loaded bronze, composition of 88.5% Cu, 9.5% Zn, and 2% Sn was polished using micromesh polishing clothes to a semi-gloss finish. Samples were then degreased using hexane, acetone, and ethanol. The following concentrations of Sigma-Aldrich BTA were allowed to completely dissolved in Fisher HPLC ethanol; 1.5, 3, 5, 30 wt.% BTA. In addition a 1.5 wt.% solution of BTA in diH_2O was prepared. Into each solution a cleaned rolled bronze sample was immersed for 1, 10, 100, and 1,000 minutes. After each immersion the sample was rinsed and dried. Two coats of Veloz microcrystalline wax was then stippled and buffed on to each of the samples. The film thickness, found using an Elcometer, ranged from 0.09 to 0.15 mils. Three additional samples of 1.5, 3.0 and 30.0 wt.% BTA in ethanol were prepared, but no additional topcoat was applied. Four additional samples of bronze with only a coat of wax, and four samples with no coating were also included in the weathering for comparison.

Each sample was initially tested using Electrochemical Impedance Spectroscopy (EIS). EIS analysis of the BTA coatings on rolled bronze was determined by application of an alternating current of 2mV to the electrochemical cell. The 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 exposed 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. EIS was measured prior to accelerated weathering conditions and denoted as “initial” when plotted.

The samples were then weathered in a Prohesion® chamber for 96 hours in accordance with ASTM G 85-94 *“Standard Practice for Modified Salt Spray (Fog) Testing”*. Samples were exposed to an environment that cycled between one hour of salt fog at 25°C and one hour of no fog at 35°C. The salt fog used for weathering was dilute Harrison solution (0.35 wt.% $(NH_4)_2SO_4$ and 0.05 wt. % NaC1 in H_20). After 96 hours of Prohesion® exposure, the bronze samples were removed, and a final EIS was measured.

Samples were also studied after weathering using digital imaging and analysis to assess the percent corrosion after weathering using the Scanalytics® software program, IPLab for Windows 2.4. A color algorithm was determined for the corrosion product, and the corrosion on each sample was identified and the overall percent corrosion was determined.

Results and Discussion

As seen in Table 1, the initial impedance readings of the samples indicate that the BTA does offer some protection. Different coating thicknesses due to different BTA concentrations, immersion times and solvents did provide varying protection before weathering. The BTA does provide initial protection to the bronze compared to the wax, indicated by the impedance values before weathering. Neither the initial nor the final impedance readings seemed to be influenced by the slight variations of the topcoat of wax. All of the BTA-Cu systems failed and bad comparable impedance to the plain wax sample after 96 hours of weathering in the Prohesion®

chamber. The results show that the samples immersed for 1000 minutes in 1.5 wt.%, 1 minute in 5.0 wt.% BTA/ ethanol, and 100 minutes immersed in 30 wt.% ethanol were top performers in the initial impedance results. After 96 days in the Prohesion® chamber all the impedances fell to relatively the same level, indicating any extra protection that the BTA was providing was lost. Of the top three samples with the highest initial impedance values, the 5 wt.% BTA/ ethanol immersed for 1 minute and the 1.5 wt.% BTA immersed for 1000 minutes both had relatively low overall percent corrosion after weathering (see Table 2). These results indicate that the BTA was providing protection to a point, but the weathering was continued past the point of failure for all the samples.

On a practical note the results of the 5 wt.% BTAI ethanol immersed for 1 minute provides encouragement for conservators, who traditionally "paint" the BTA solution onto the bronze. It would be feasible impossible for a conservator to reproduce the film of a 1000 minute immersion by brushing the BTA onto a large statuary. Additionally important to conservators is the surface appearance. One of the main requirements of a conservator is to treat an object without changing the aesthetics of the piece that is being treated. The BTA 3,5,and 30 wt.%, and the 30 wt.% BTAI ethanol immersed for 100 minutes changed the surface appearance of the polished bronze to cloudy and iridescent, which would be considered unacceptable change.

Another significant observation is that water was not a good solvent for the BTA. The 1.5 wt.% BTAI water is the highest concentration of BTA that stays in solution at room temperature. This 1.5 wt.% solution had very low initial and final impedance values and had a very high overall percent corrosion value after weathering.

Conclusions and Future Work

The initial impedance readings of the samples indicate that the BTA does offer some protection, and the different Cu-BTA thicknesses due to different solvents immersion times and concentrations do provide varying protection. The reason for the different behavior is not yet understood. Although the Cu-BTA + wax system did not provide "acceptable" levels of protection after 96 hours of weathering in the Prohesion Chamber, the study did reveal that different Cu-BTA coatings can have significant initial resistance to the Harrison solution. It was found that 5 wt.% BTA/ ethanol immersed for 1 minute was one of the top performers when evaluating the initial impedance readings, and had a relatively low overall percent corrosion. This is an encouraging find for the practical application of BTA solutions on sculpture. Another significant observation was that water is not a good solvent for BTA and the BTAI water solutions resulted in lower initial impedance values. Ethanol, which readily dissolves the BTA at the lower concentrations, should be used in place of water as the solvent. This initial work suggests that the concentration and immersion time play a significant role in the performance of the Cu-BTA coating in corrosion protection. There seems to be conditions that optimize the Cu BTA film growth, producing a more resistant film. According to the study there is not a linear correlation between the coating performance and the film thickness. It would be beneficial to continue this research on cast bronze, which is more representative of the majority of outdoor sculpture, and to run EIS on the samples throughout the weathering period, to better understand the failure point.

Table 1
Z modulus (ohms) at 0.1 Hz
of Rolled Bronze + Coating Before and After Weathering

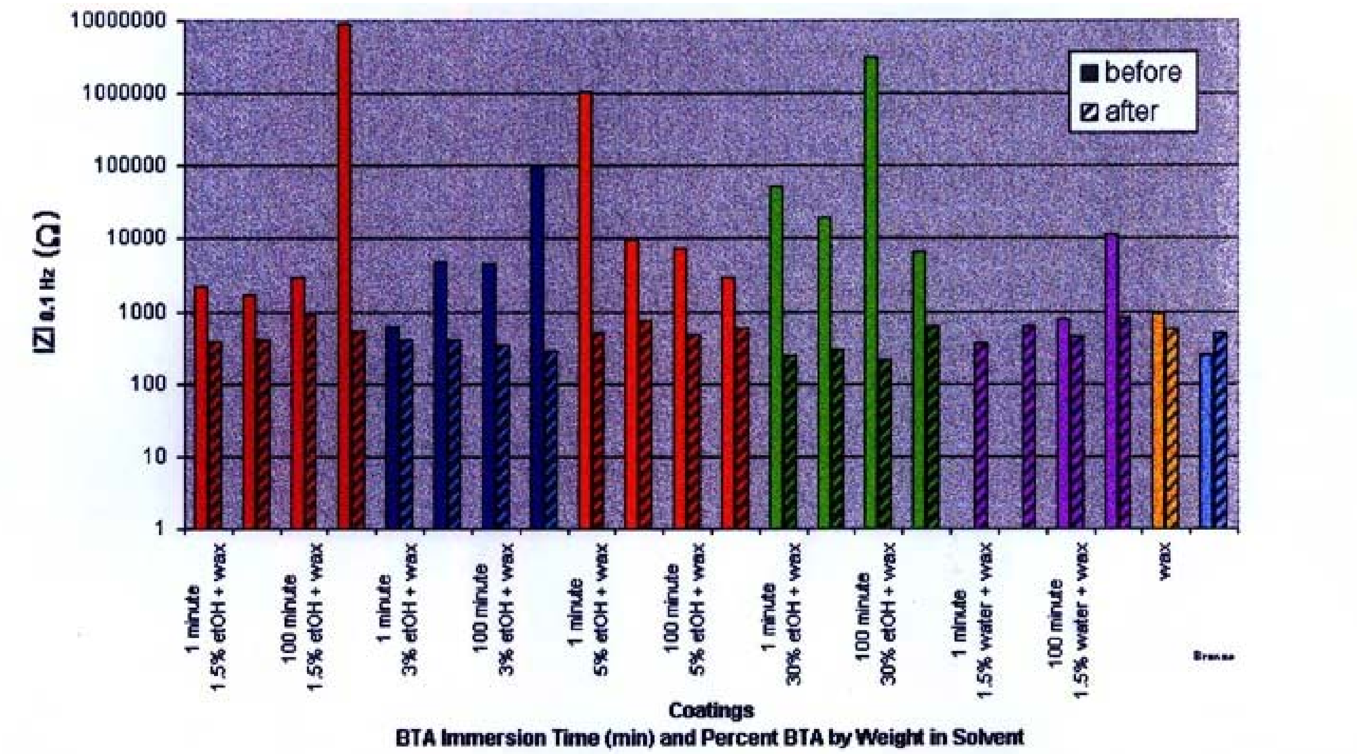


Table 2
Percent Corrosion After Weathering on Rolled Bronze Samples Found by Digital Imaging Analysis

	1 minute immersion	10 minutes immersion	100 minutes immersion	1000 minutes immersion
1.5% BTA/ etOH + wax	92.57	93.6	80.6	34.64
1.5% BTA/ etOH	98.23			
3.0%BTA/ etOH + wax	99.21	80.23	92.35	99.91
3.0% BTA/ etOH			99.97	
5.0% BTA/ etOH+ wax	48.47	65.66	44.56	99.99
30.0% BTA/ etOH + wax	98.58	93.63	99.10	99.99
30.0% BTA/etOH				95.84
1.5% BTA/ water + wax	99.96	99.92	99.99	99.99

References

[14] Sease, Catherine, “Benzotriazole: A review for Conservators”, *Studies in Conservation*, 23 (1978), 76-122.
[15] Madsen, Brinch H, “A Preliminary Note on the Use of Benzotriazole for Stablizing Bronze Objects”, *Studies in Conservation*, 12 (1967), 163.
[16] Sease.
[17] Brostoff, Shedlosky, and de la Rie, “External Reflectional Study of Copper-Benzotriazole (Cu-BTA) Film Growth on Bronze in relation to BTA Pretreatments for Coated Outdoor Bronzes” IIC proceedings 2000, not yet published.

Appendix B

Protocol for the Characterization Of the Corrosion Protective Properties Of Coatings Over Bronze

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

2. Project title: Development and Testing of Organic Coatings for the Protection of Outdoor Bronze Sculpture from Air-Pollutant Enhanced Corrosion – Year 1

Application of the electrochemical impedance spectroscopy technique has been incorporated into the protocol for the characterization of the corrosion protective properties of coatings over bronze samples. This electrochemical technique along with accelerated weathering exposure conditions has provided quantitative data to be acquired to aid in the assessment of multiple coatings on bronze.

Accelerated weathering of the samples occurred through the use of both a Prohesion fog and QUV chamber. Samples underwent cyclic exposures in accordance with ASTM D 5 894-96 "*Standard Practice for Cyclic Salt Fog/UV Exposure of Painted Metal (Alternating Exposures in a Fog/Dry Cabinet and a U V/Condensation Cabinet)* ". Samples began accelerated exposure in the QUV cabinet for one week where conditions consisted of four hours of exposure to 340 nm UV-A at 60°C, alternated with 4 hours of condensation at 50°C. After seven days of QUV exposure, samples were removed and electrochemical impedance spectroscopy was used to measure the impedance of the coatings. After electrochemical testing, samples were placed into the Prohesion chamber for seven days. Conditions in the chamber consisted of an environment that cycled between one hour of salt fog at 25°C and one hour of no fog at 35°C. The salt fog used for weathering was dilute Harrison solution (0.35 wt. % $(NH_4)_2SO_4$ and 0.05 wt. % NaC1 in H_2O). The test cycle is shown schematically in Figure 1 below.

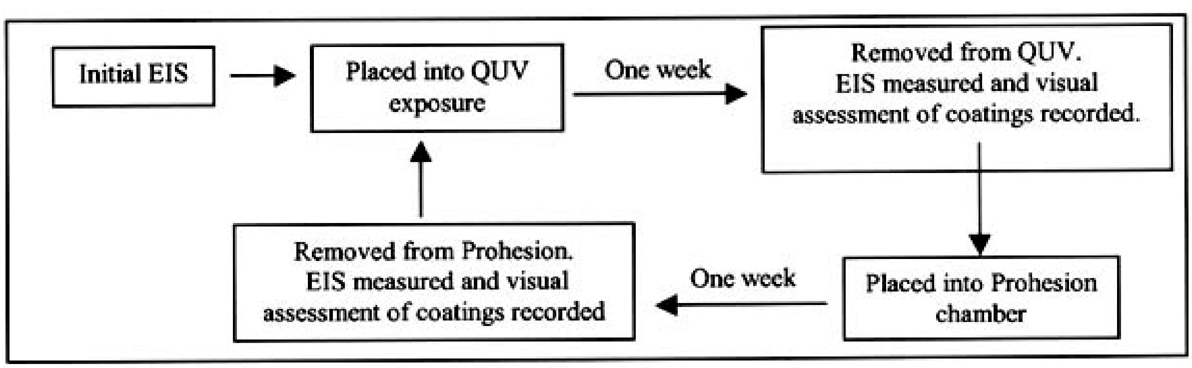


Figure 1: Prohesion/QUV cycling and EIS Protocol

The amount of exposure time varied depending on the corrosion performance of the coatings. The low performance coatings on bronze were removed from accelerated exposure after only 14 days of exposure, while high performance coatings remained in accelerated conditions for over 250 days. All samples remained in accelerated testing until EIS data indicated that the coating systems were providing little corrosion protection over the bronze substrate.

Electrochemical impedance spectroscopy (EIS) was incorporated into this protocol to acquire quantitative measurements of the corrosion protection properties of the coatings. ElS 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.