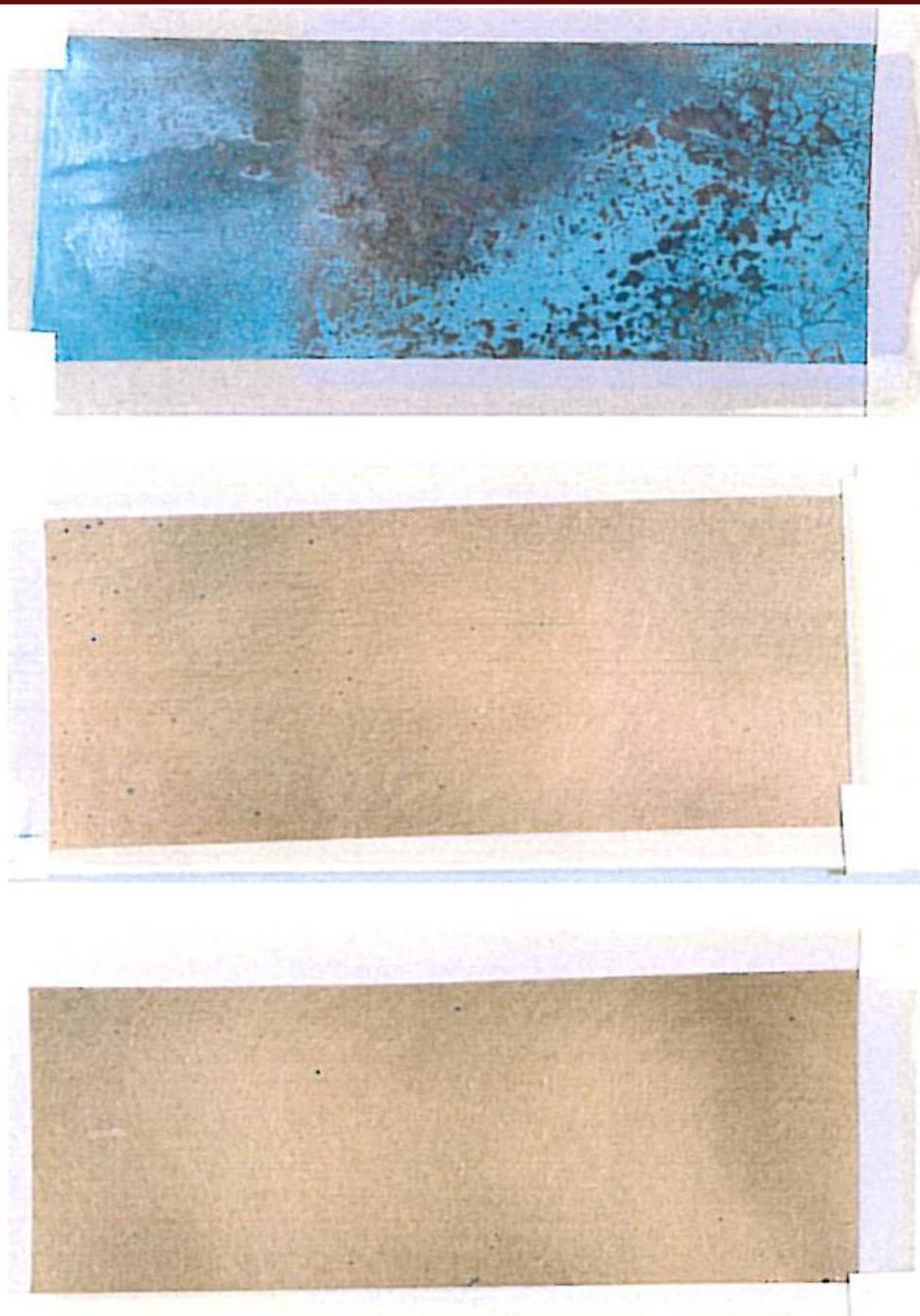




Development and Testing of Organic Coatings for the Protection of Outdoor Bronze Sculpture from Air-Pollutant Enhanced Corrosion: Year 3 | 2002-18

North Dakota State University



National Park Service
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Executive Summary

The third year of research focused on the evaluation of experimental and currently used coating systems on both polished and patinated bronze substrates. This work used accelerated weathering to further evaluate the coatings performance. Electrochemical means of analysis as well as color measurement, gloss, surface energy and coating thickness were used to monitor the aging of the weathered films throughout the weathering process.

Improved protective coatings are needed for outdoor bronze sculpture and ornamentation. Previous research has shown that the most protective coatings tend to be impervious to conventional solvent removal techniques and standard mechanical removal methods damage bronzes and their patinas. This study evaluates new solvent removable coatings and compares their protection to the currently used systems.

Introduction

Bronze is one of the most popular materials used in outdoor 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 as possible in an 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 threats of moisture, heat, oxygen, ultraviolet, and biological attack, suffer irrevocable changes from damaging and scarring corrosion.

For these reasons various protective coatings were tested on two types of bronze panels and exposed to accelerated weathering. Coatings provide a barrier between the corrodants and the metal substrate. By various mechanisms the coating system inhibits corrosion. Advanced spectroscopic and electrochemical methods were used to characterize new coatings candidates with respect to ultraviolet (UV) resistance and corrosion resistance.

The protection afforded to the bronze panels were monitored by two separate electrochemical methods, electrochemical impedance spectroscopy (EIS) and electrochemical noise methods (ENM). Using the information from both of these techniques one can monitor the coating after certain timeframes of accelerated weathering. Other methods of monitoring the coatings were also employed including monitoring color change, the change in gloss, the thickness of the coatings, and the surface energy of the coatings. As a material is weathered it is expected that each of these properties will change over time. A coating that is able to withstand the weathering process will delay changing longer than those coatings not able to withstand the weathering process as well.

This work is an attempt to increase the available options of coatings for the conservator of outdoor bronze works. 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 Inralac[®] 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.

Experimental Methods

Bronze 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 inch 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.

Coatings

The polyvinylidene fluoride PVDF that is being explored is Kynar[®] RC-10,052 PWD PVDF, made by Autofina. The PVDF is a hexafluoropropylene- vinylidene 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, was blended the copolymer with an acrylic polymer. The acrylic used was Paraloid A-21, which is an acrylic resin made by Rohm and Haas. 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. A 8% mixture of Autofina's KYNAR[®] 1005 in acetone and solution of 40% of Rohm and Haas' acrylic Paraloid A21 in toluene was mixed in a 30 to 70% ratio. This coating will be referred to as "FLC + A21".

Inralac[®] was developed in the 1960s by the International Copper Research and Development Corporation in New York. The base of Inralac[®] is the resin Paraloid B-44 made by Rohm and Hass Inc, which is an ethyl methacrylate/methyl methacrylate copolymer. In addition to Paraloid B-44, Inralac[®] 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. This coating without a pretreatment will be referred to as "Inralac". The

samples that were pretreated with BTA and then have a topcoat of Inralac will be referred to as "BTA + Inralac".

The different samples weathered are listed below in Table 1.

Table1. Sample descriptions

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

Substrate Preparation and Coating Application

Each sample was made in triplicate on cast polished bronze and French brown patinated bronze. 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 Table1, 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 ENM.

Monitoring

In between each week of accelerated 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 made by Elcometer Inc.ⁱ The color of each sample was obtained using a Microflash® made by Datacolor Internationalⁱⁱ and the L*, a*, b* of each was recorded. The contact angle of each sample was obtained using a dynamic contact angle analyzer, FTÅ 125, made by First Ten Ångstromsⁱⁱⁱ. The gloss readings were analyzed using Novo-gloss™ Model number made by Gardco® Paul N. Gardner Company, Inc.^{iv} at 20, 60 and 90 degrees.

The glass transition temperatures (T_g) are an important indicator of the properties a polymer will have. The glass transition temperature is defined as the point at which the thermal expansion coefficient increases.² On an atomic level the glass transition temperature can be described as the temperature in which “holes” between molecules are large enough that neighboring molecules or parts of a polymer chains can fit within the spaces.² Hence as the temperature is increasing at a fixed rate, the volume the molecules occupy also increases at a set rate, but once the glass transition temperature is reached there is a greater increase of volume. A method of measuring the glass transition temperature is by using a differential scanning calorimetry (DSC). One of the physical properties that can be derived from the glass transition temperature is the polymer backbone flexibility. If the polymer is very flexible the T_g would be lower than a polymer with a very rigid backbone. DSC was run to identify the glass transition temperature (T_g) for each polymer. The T_g was found using a TA Instruments^v DSC Q 1000 ramped at 10°C/ minute.

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 cm². A Gamry^{vi} PC3 potentiostat with CMS 100 software was used to collect the data over the frequency range of 5000 to 0.1 Hz. For the ENM, 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 (R_n) is derived. A total of four samples were compared, and the noise between *each* of the panels was monitored.³

ⁱ Elcometer Inc, 1893 Rochester Industrial Drive, Rochester Hills, Michigan 48309. USA

ⁱⁱ Datacolor International, 5 Princess Road, Lawrenceville, NJ 08648.

ⁱⁱⁱ First Ten Angstroms, Vernon G. Eberwine, III, 465 Dinwiddie Street, Portsmouth, VA 23704.

^{iv} Paul N. Gardner Company, Inc., 316 N.E. First Street, Pompano Beach, FL 33060.

^v TA Instruments 109 Lukens Drive New Castle, DE 19720.

^{vi} Gamry Instruments, 734 Louis Drive, Warminster, PA. 18974.

Weathering

To identify the weathering of the above mentioned coatings on two different substrates, these systems were exposed to an artificial weathering scheme for 11 weeks in accordance consisting of Prohesion^{®vii} and exposure in the QUV^{®vii} 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)*.

This weathering protocol begins with 7 days in QUV[®] chamber which cycles between 4 hours at 50°C during the dry cycle and 4 hours at 60°C during the wet cycle with UV exposure. The weathering is then followed by 7 days in Q-Fog Prohesion which consists of 1 hour at 35°C, dry, and 1 hour at 35°C during a fog cycle is run. The fog is made up of Dilute Harrison's Solution which is 0.35 wt% (NH₄)₂SO₄, and 0.05 wt.% NaCl in water.

Results and Discussion

Electrochemical Tests

Electrochemical methods such as EIS and ENM are techniques that provide a quantitative analysis of a corroding material.^{3,4,5,6,7,8,9,10,11} As mention in the above discussion, when measuring the R_n one is able to measure the resistance without perturbing the system with applied voltage or current. Figure 1 is the average R_n vs. Time of weathering. This diagram of the R_n vs. Time indicates that initially the three distinct coatings on the polished bronze provide very similar protection to the substrate. After the first two weeks of accelerated weathering the R_n of the Incralac sample on polished bronze decreases more quickly than that of the FLC +A21 or the BTA + Incralac. The two later coatings have a slower decay in their R_n indicating a higher protection afforded to the bronze substrate for a longer time. There is a significant difference in the R_n between the systems on polished bronze vs. the patinated bronze substrate. The explanation for the severe discrepancy is explained in Figure 6. Because of the porosity of the substrate, the film thickness of the patinated bronze Incralac system seems to have decreased rapidly. It is the opinion of the authors that the coating was absorbed by the substrate. Therefore, even though an equal amount of material was applied to the substrate, much less material was sitting above the surface to act as a barrier. It is thus suggested that multiple coating be tested for this type of substrate in future tests. The R_n of the two uncoated samples increased slightly over time. This result, although seemly unexpected, is due to a build up of corrosion. The corrosion product acts like a barrier layer, and thus the R_n for these two samples increased slightly over time.

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

^{vii} Q-Panel Lab Products, 800 Canterbury Road, Cleveland, OH 44145

film resistance. Figure 2 is the initial Bode plot for a typical sample of each of the coating systems. This data also indicates that initially the BTA+ Inralac and the FLC + A21 samples on polished bronze have good resistance. The polished and patinated Inralac samples are a decade lower in their impedance, suggesting a slightly lower resistance to the electrolyte. The uncoated samples impedance can be thought of as the failure point of the coating, when the coating no longer is protecting the system.

Figure 3 is the Bode plot after seven weeks of accelerated weathering. The FLC + A21 on the polished surface after seven weeks of weathering has not changed resistances, indicating that an uniform and intact coating system still exists on the sample. The low frequency impedances of the BTA + Inralac sample on the polished bronze and the Inralac in the polished bronze have both decreased a power of ten. This indicates that the system has been compromised by the weathering process, but is still providing adequate protection. The Inralac sample on the patinated bronze is performing significantly worse and is approaching the failure point. Again the increase in the low frequency impedance of the uncoated samples is due to the build up of corrosion product.

After 11 weeks of exposure, the low frequency impedance of both the BTA + Inralac and the FLC + A21 have decreased to around $10^{6.5} \Omega \cdot \text{cm}^2$ indicating that the systems are starting to fail.

The electrochemical tests seem to indicate that the pretreatment of the substrate with the BTA pretreatment significantly increases the lifetime of the coating.

Glass Transition Temperatures (T_g)

The glass transition temperatures of the coatings were tested and can be found in Table 2.

Table 2. Glass Transition Temperatures of the various coatings

| Sample | T_g ($^{\circ}\text{C}$) |
|--------------------------|------------------------------|
| Inralac | 62 |
| Inralac after weathering | 62 |
| Fluorocarbon | 41 |
| Paraloid A21 | 100 |
| FLC + A21 | 50 |

The T_g of the coatings and the component polymers for the coatings were monitored to see if the weathering protocol had an effect on the coating system. It appears that the Inralac has not been changed by the accelerated weathering. The results of the FLC + A21 after weathering were not discernable and still need to be reexamined.

Color change

The color change over time was monitored using the Commission Internationale de l'Eclairage (CIE) $L^* a^* b^*$ system to monitor changes. Using this system a ΔE of 0.1 is a perceivable color change. ΔE is determined by the following equation:

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$$

Where L^* , a^* and b^* are separate axis representing in the CIE $L^*a^*b^*$ color system. The axis provide a numerical means of describing the color. The ΔE over time of weathering for each of the polished bronze samples is seen in Figure 5. The uncoated sample's ΔE is significant after 1 week of weathering. The coated samples did show a slight color change over time.

Film Thickness

The average film thickness of each type of coating is shown in Figure 6. The coated polished bronze samples all slightly decreased in film thickness over time. The patinated bronze Incralac sample had a significant decrease in the film thickness over the 7 weeks it was weathered. This decrease in film thickness is most likely the source of the poor performance of the Incralac on the patinated sample. After weeks 2 and 3 of weathering the film growth of the patinated Incralac sample increased significantly. This is believed to be a result of actual film growth, but rather due to the formation of corrosion product.

Contact Angle

As seen in Figure 7, the contact angle of the coated systems decreases with time. This increase in the surface energy, resulting in a smaller contact angle, with weathering is expected. The contact angle the uncoated samples rapidly decreases. The linear regression of the contact angle of the polished FLC + A21, polished BTA + Incralac, and patinated Incralac decrease parallel to each other. The linear regression of the polish Incralac sample does not have as significant of a negative slope. Contact angles have been used previously to predict lifetime of a coating system. According to this property the BTA + Incralac and the Incralac sample, both on polished bronze have reversed performance positions.

Substrate Characterization

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. The digital images through out the weathering regime, of a representative panel for each of the system types, are found in Figures 8-15. It is very apparent visually how quickly the uncoated panels corrode. After 1 week of exposure corrosion is present. After 2 weeks of weathering the uncoated panels are significantly corroded and the patinated Incralac sample has a significant percentage of its face covered in corrosion product. After 6 weeks of weathering both the Incralac and FLC+ A21 samples on polished bronze show a slight amount of corrosion

product. Testing was continued on these two series because the electrochemical data indicated that protection was still being afforded to the metal.

Conclusions

The electrochemical studies indicate that the fluorocarbon-acrylic blend has the potential of being an excellent coating. The poor adhesion of the coating was indicated by the decrease in the R_p . The Bode plots of the system still indicate the FLC + A21 on polished bronze as a very good barrier coating. If the adhesion of the fluorocarbon could be increased, it would prove to be a very good alternative for conservators. The BTA pretreatment + topcoat provides significantly more protection than without the pretreatment. It is thus recommended that BTA pretreatments be maintained under a protective topcoat. It is still in question whether the increase lifetime of the BTA pretreated samples were due to the extra protection afforded by the BTA, or if it was due to the higher initial film thickness. ENM seems to reflect coating performance based on the coating thickness compared to results found by EIS. It is maintained that both electrochemical tests should be run to get a larger scope of what is occurring in the coating-metal system. The patinated sample had a very porous surface. Even though an equal amount of coating was applied to the patinated surface as well as the polished bronze surface, it seems that the patinated surface absorbed a significant amount of the coating and therefore resulted in a thinner coating, and thus it was less protected, as seen in the electrochemical results, compared to its polished bronze counterpart. Therefore in future studies, the absorption of the coating into the surface needs to be considered when determining the appropriate thickness of the coating. It is concluded by the authors that the need for a more durable coating with good adhesion still exists.

Future Work

Coatings that are not necessarily removable by solvents need to be explored as possibilities for coating bronze. It has been shown in this and previous studies^{12, 13, 14, 15}, that by only using materials that are solvent removable the performance of the coating systems as well as the functional life of the coating is limited. A system of removing the coatings will also need to be developed in hand with the coating itself.¹⁶

Acknowledgments

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Figure 1. Average Sample Noise Resistance vs. Time

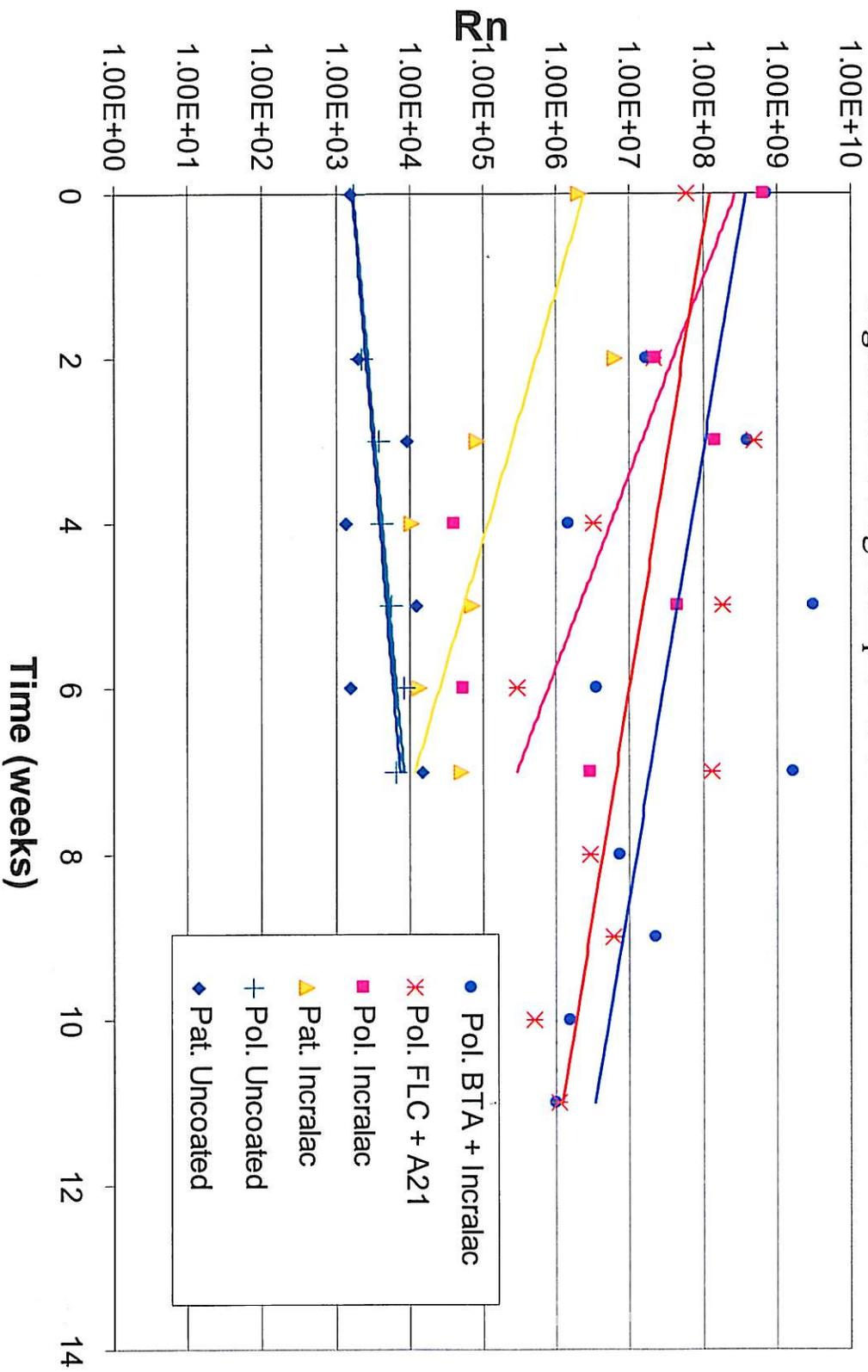


Figure 2. Initial Bode Plot

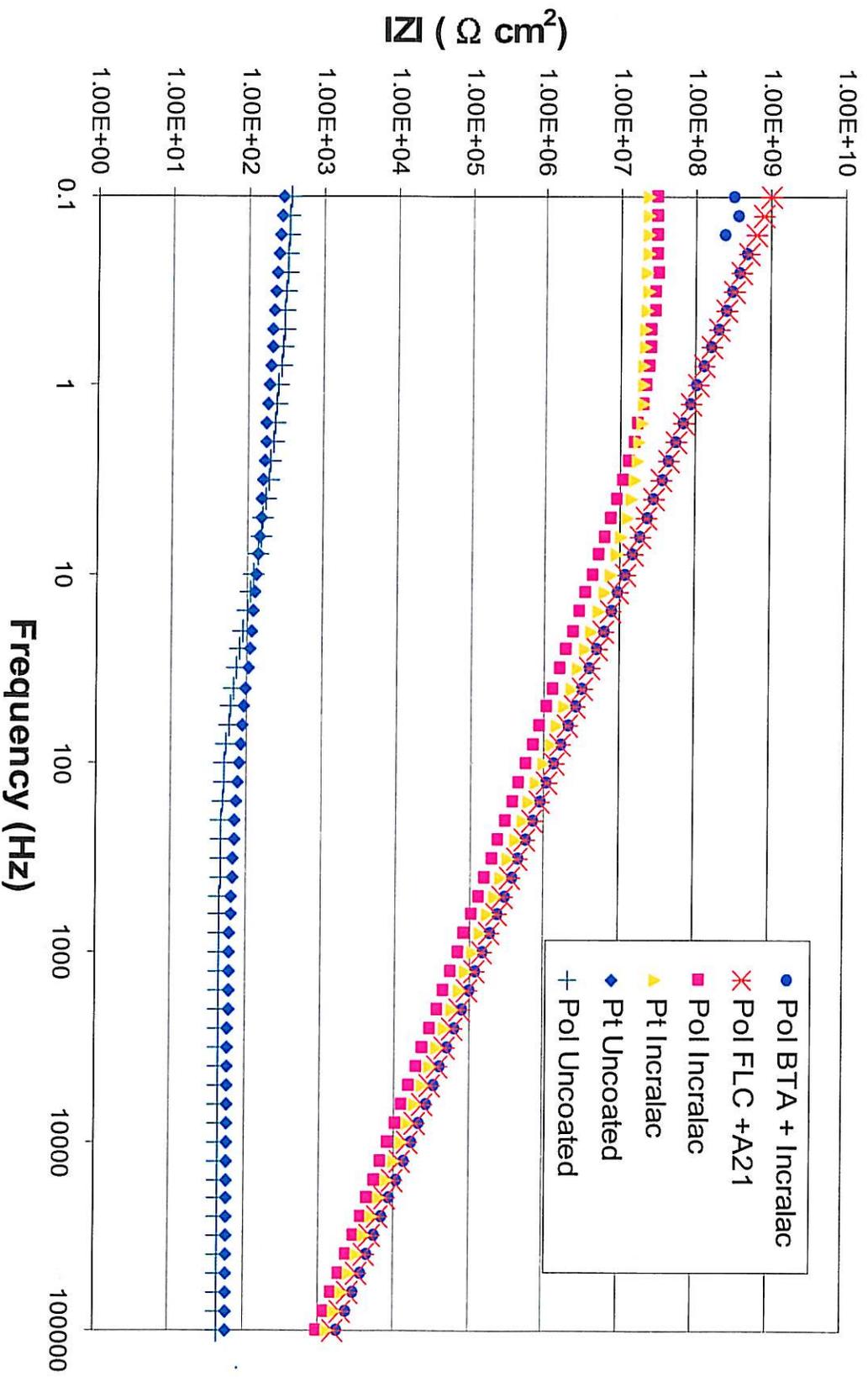


Figure 3. Bode Plot after 7 weeks

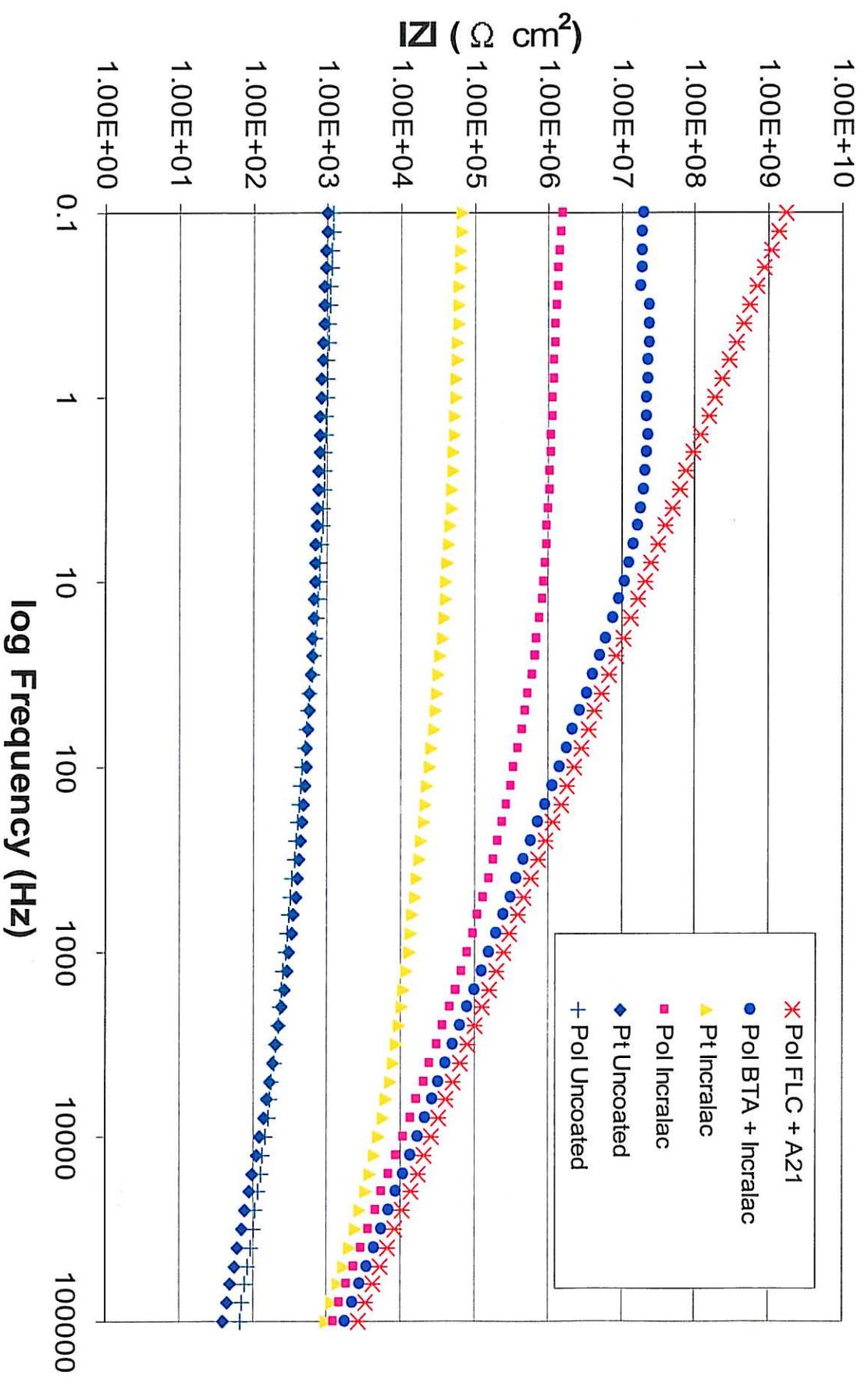


Figure 4. Bode plot after 11 weeks of exposure

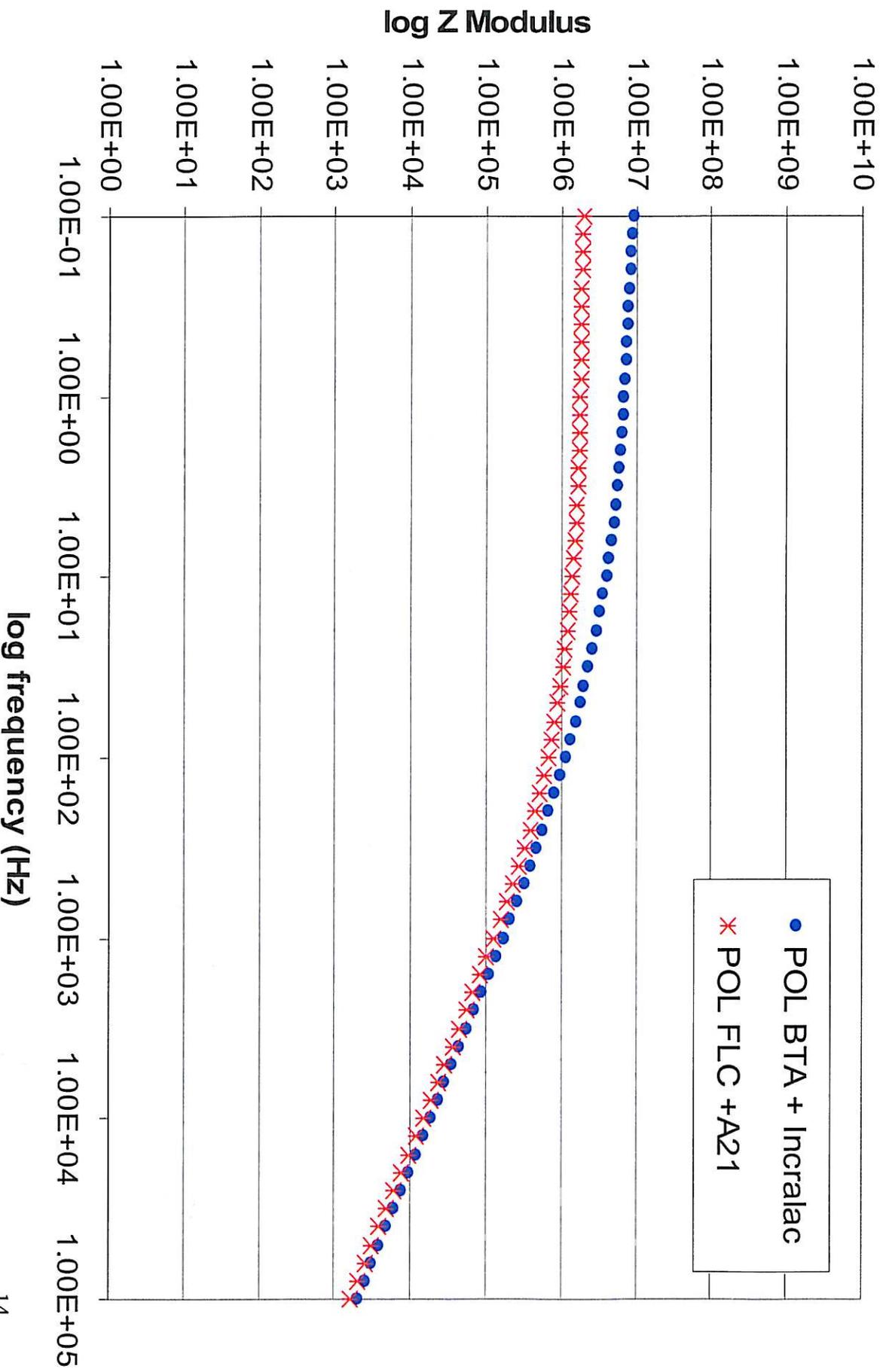


Figure 5. Delta E vs. Time

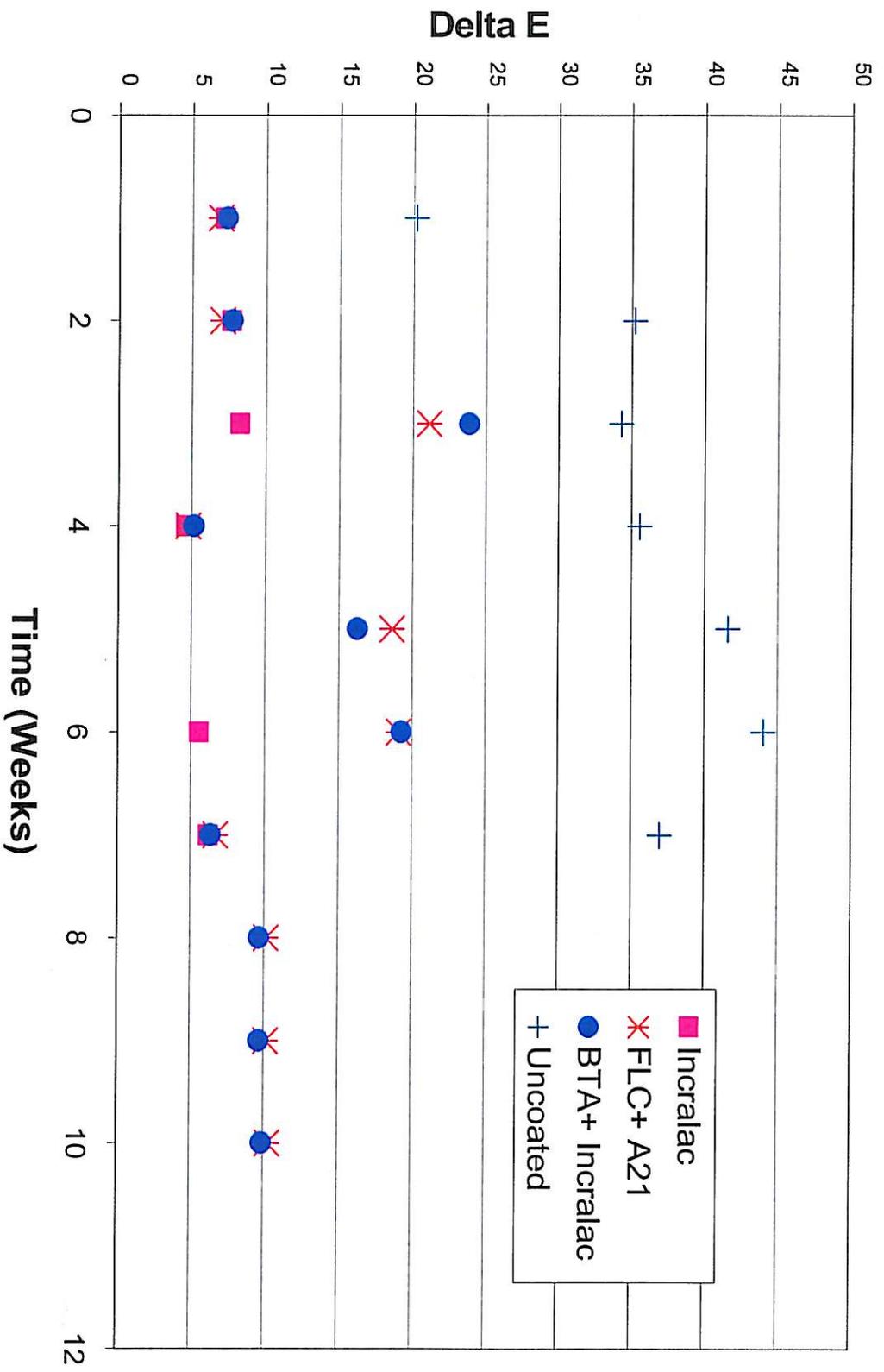


Figure 6. Average Film Thickness vs. Time

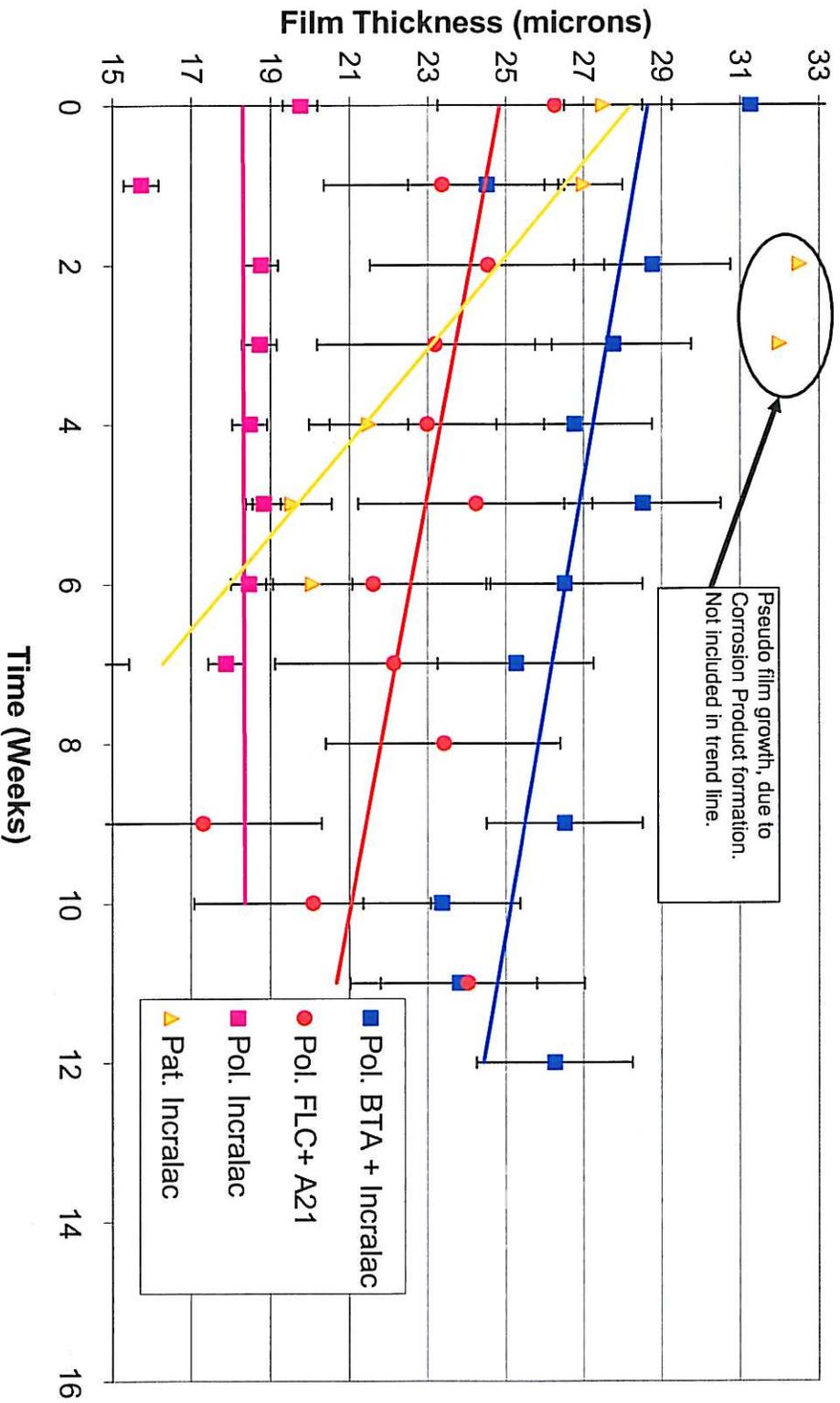


Figure 7. Average Contact Angle vs. Time

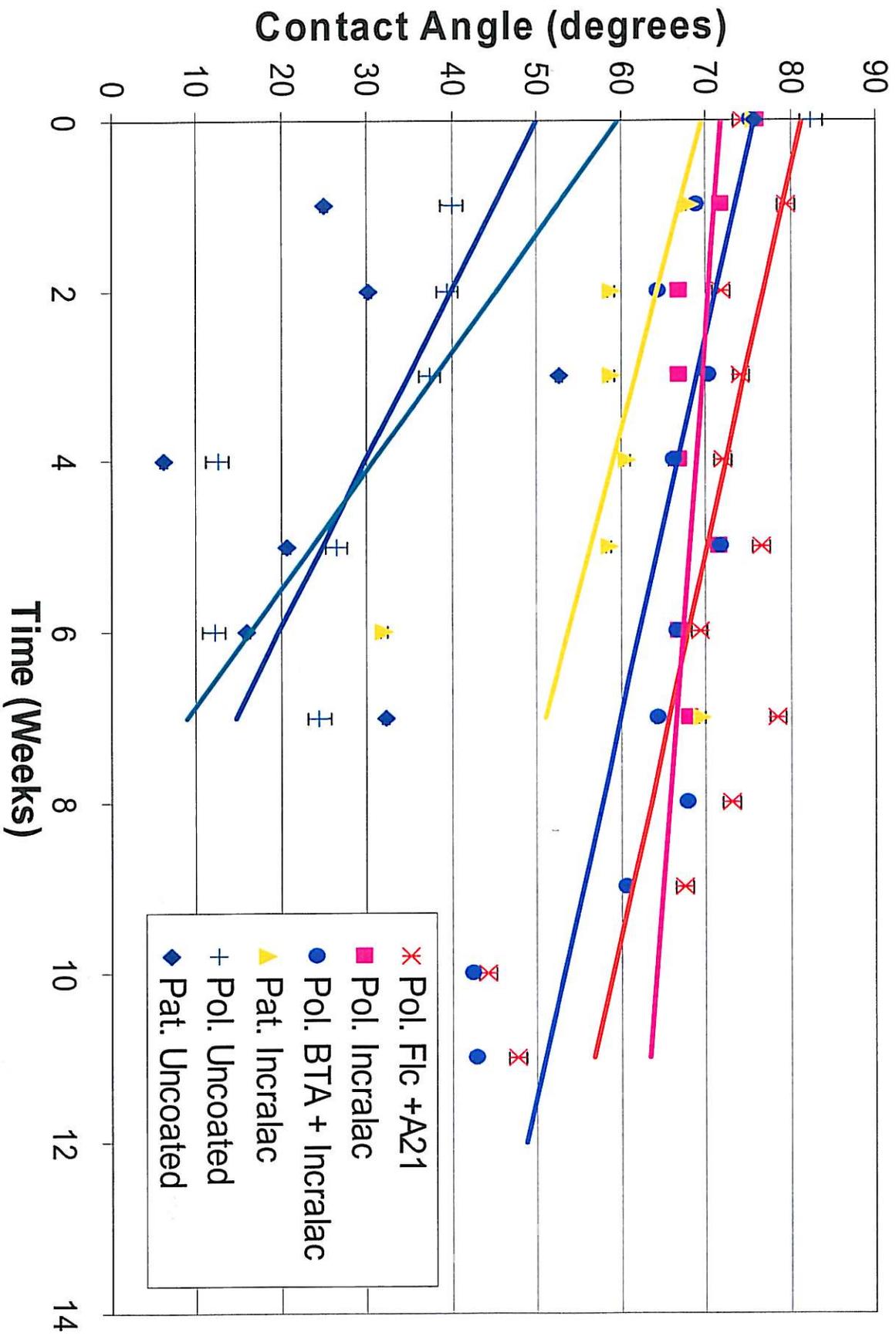


Figure 8. Images of representative panels without weathering.

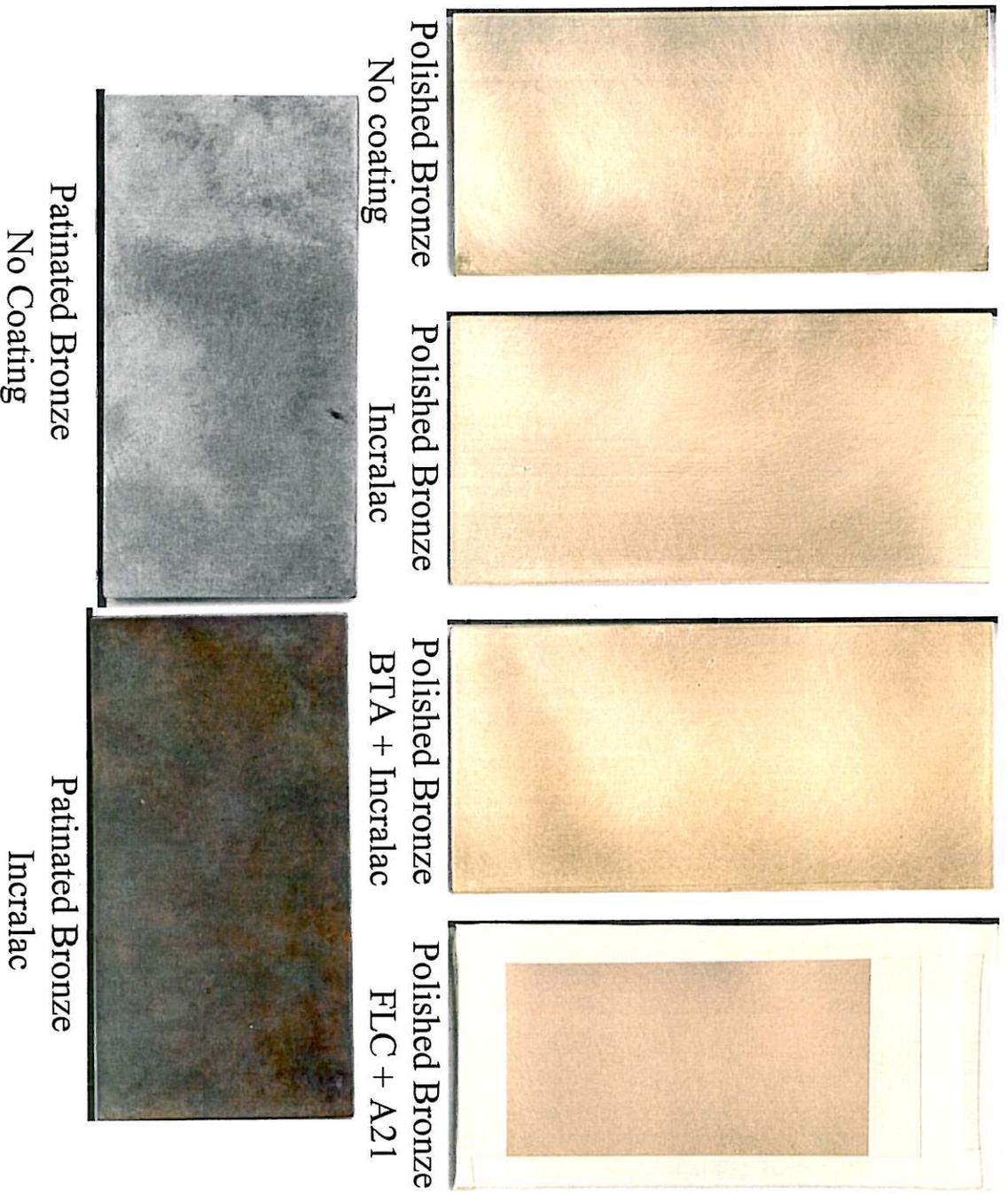


Figure 9. Images of representative panels
After one week of weathering.

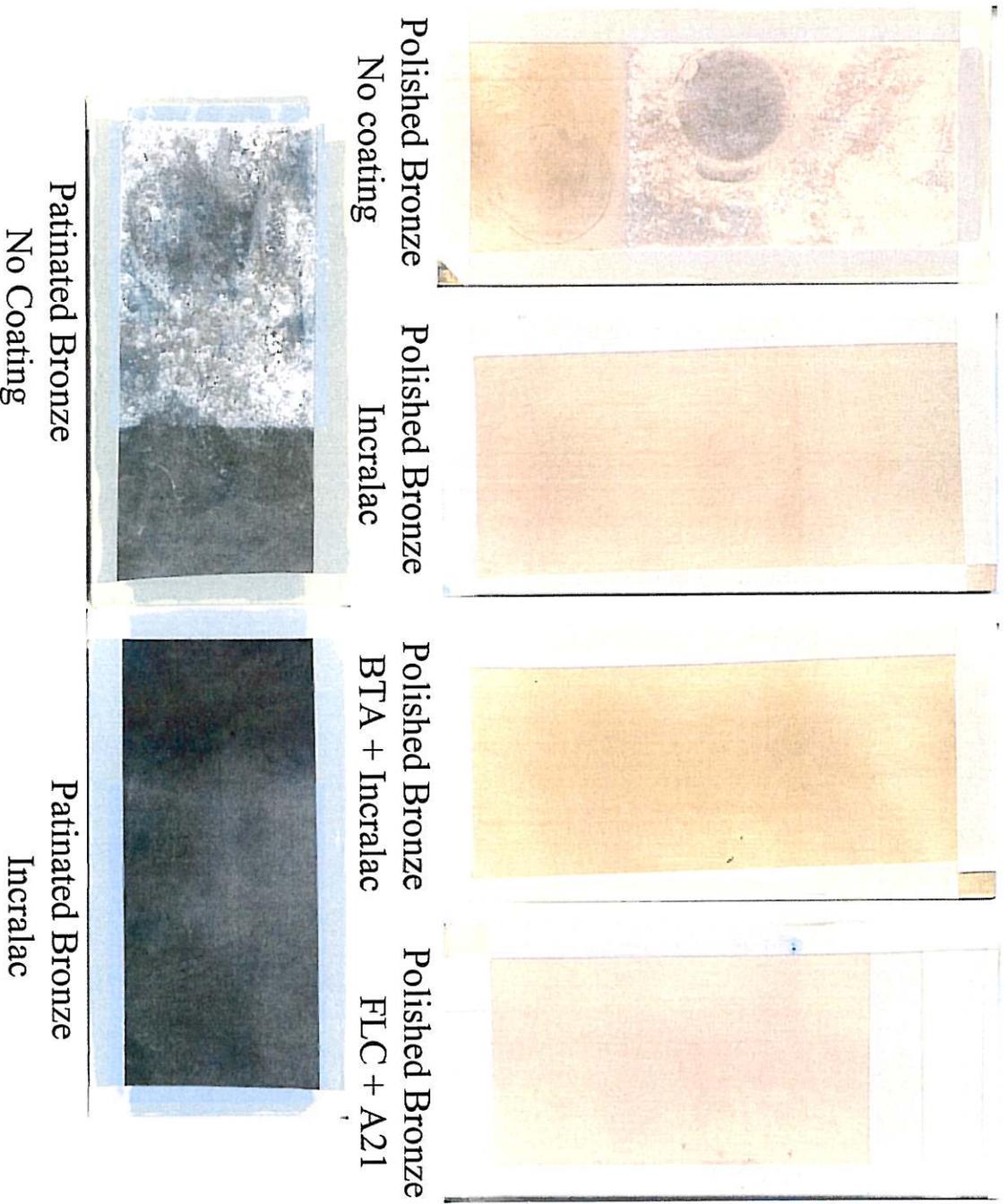


Figure 10. Images of representative panels
After 2 weeks of weathering.

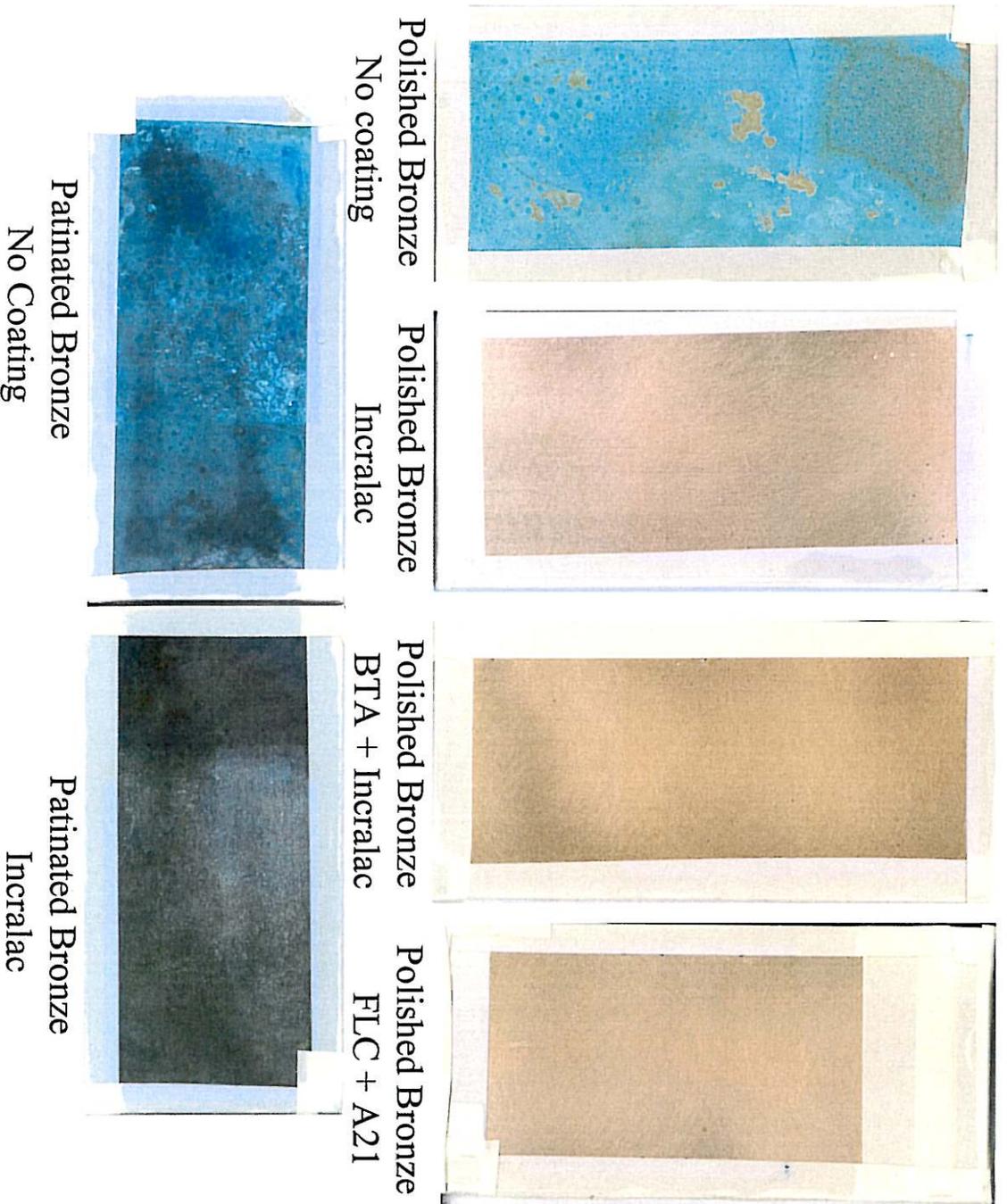


Figure 11. Images of representative panels
After 3 weeks of weathering.

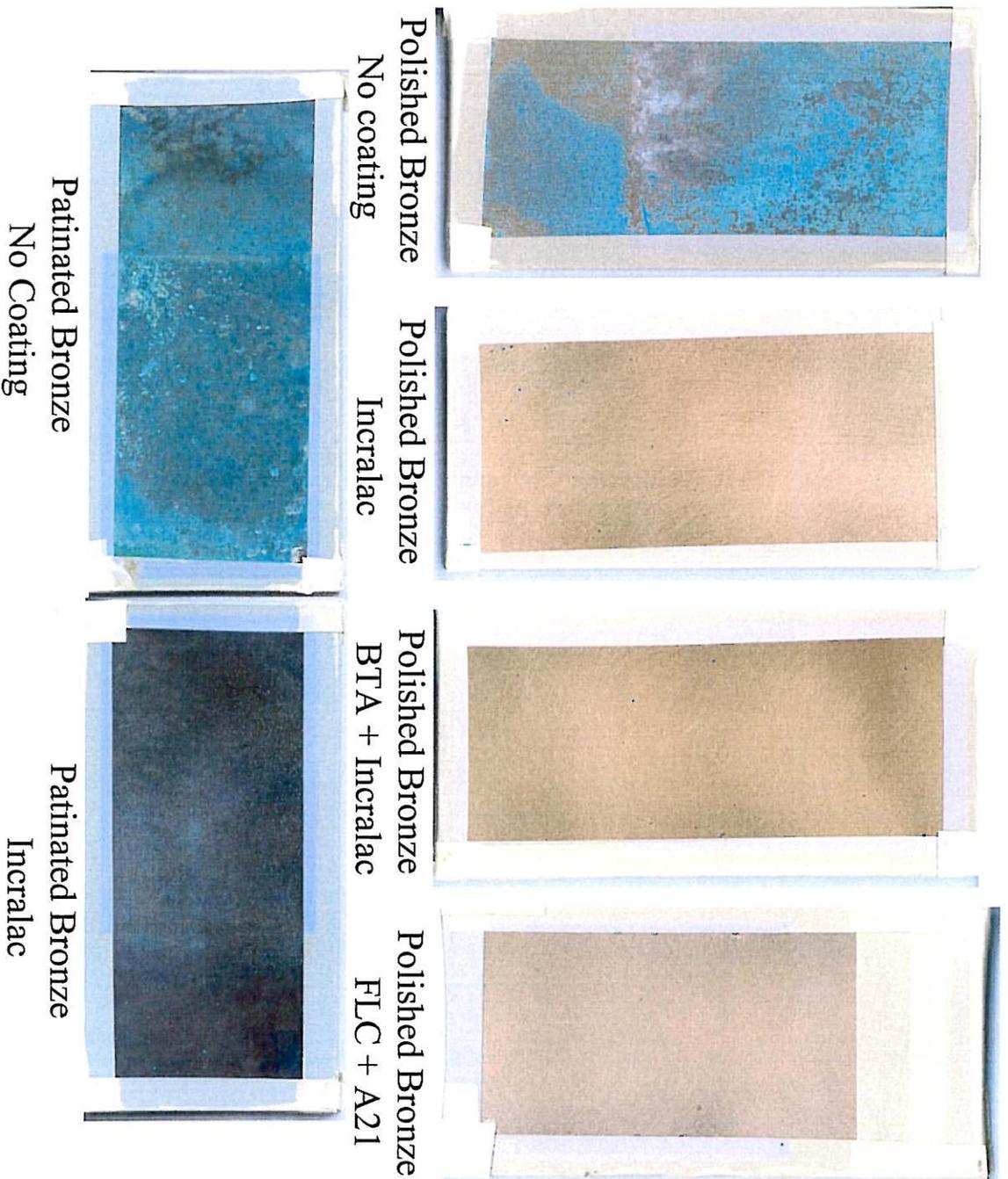


Figure 12. Images of representative panels
After 4 weeks of weathering.

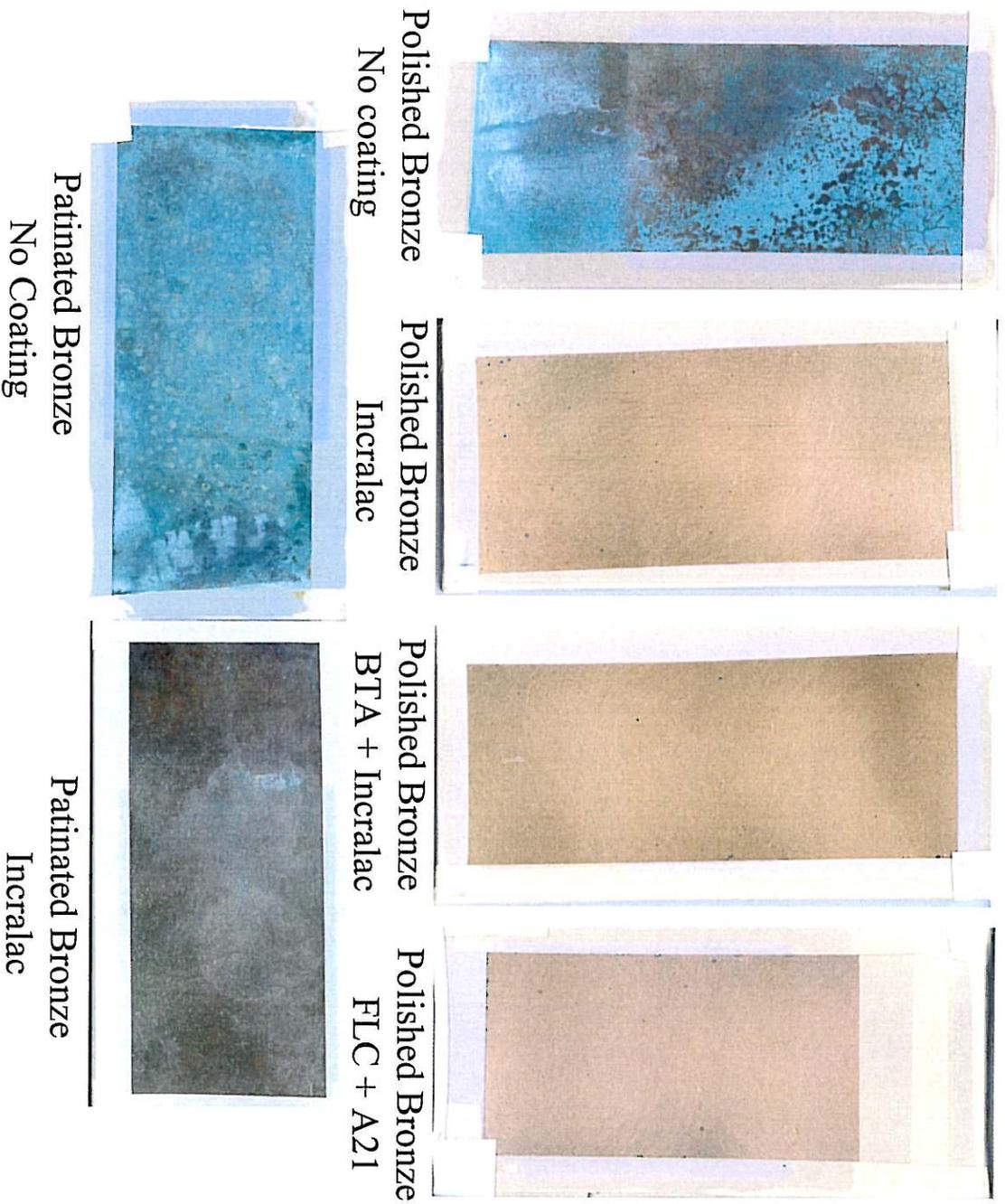
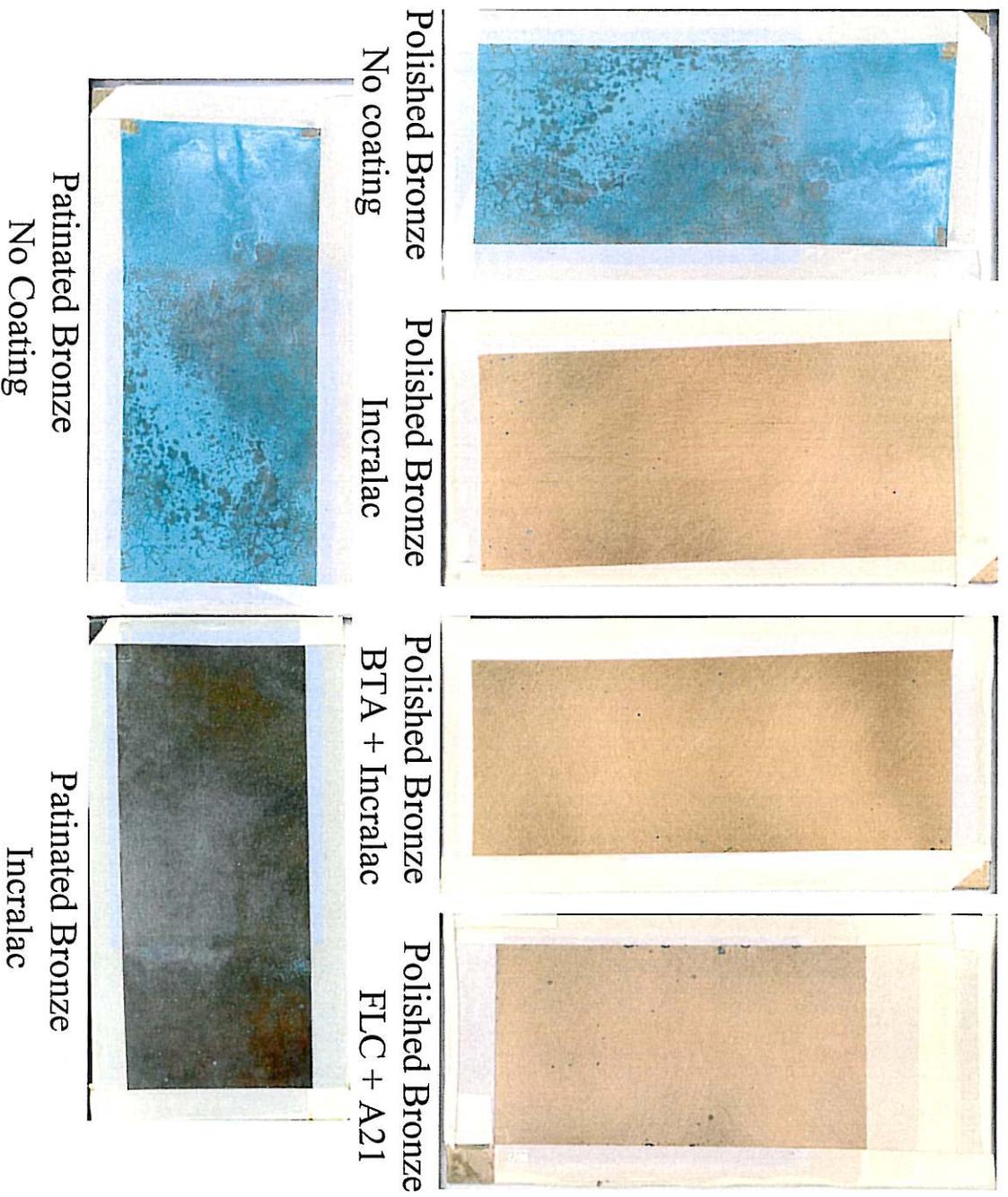


Figure 13. Images of representative panels
After 5 weeks of weathering.



**Figure 14. Images of representative panels
After 6 weeks of weathering.**

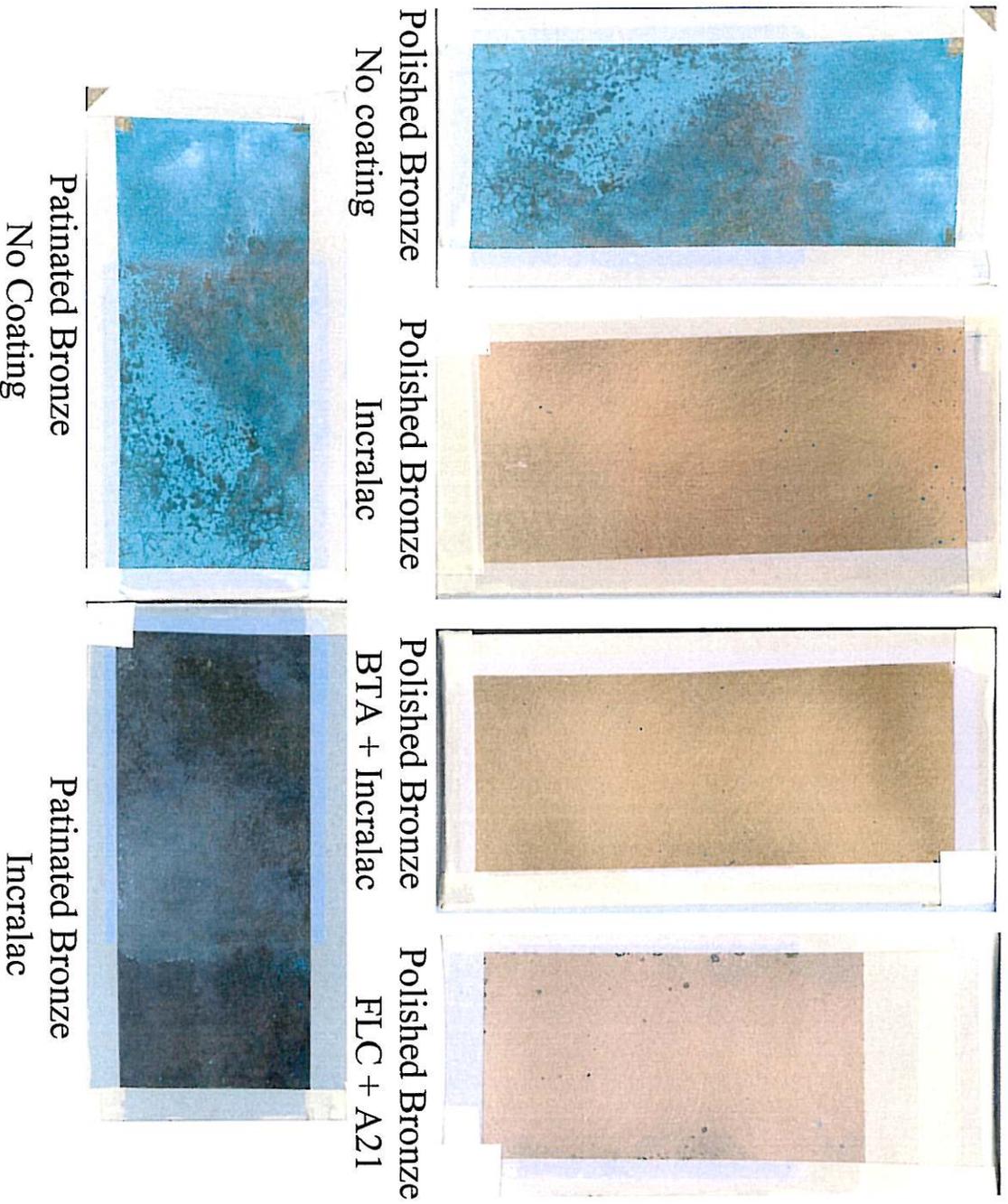


Figure 15. Images of representative panels after 7 weeks of weathering.

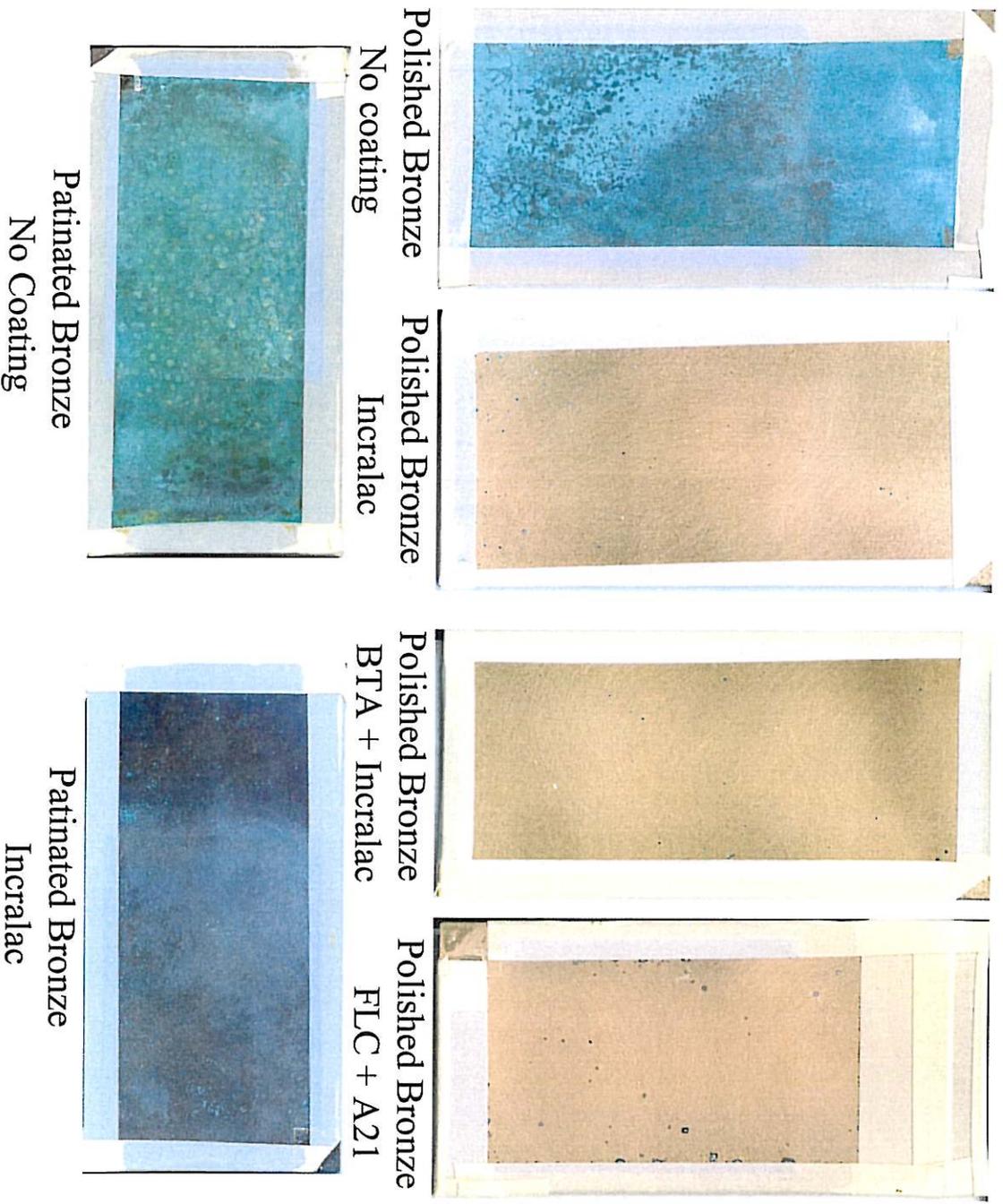
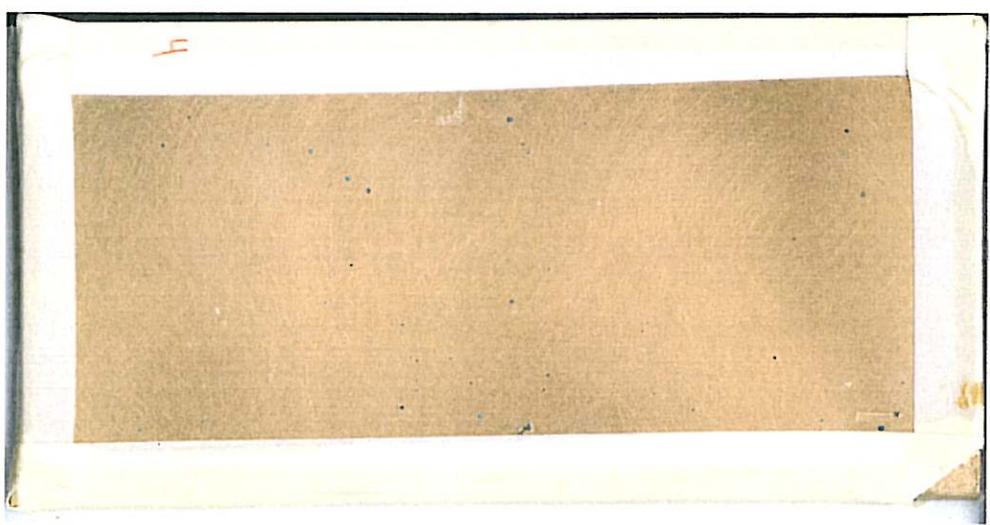
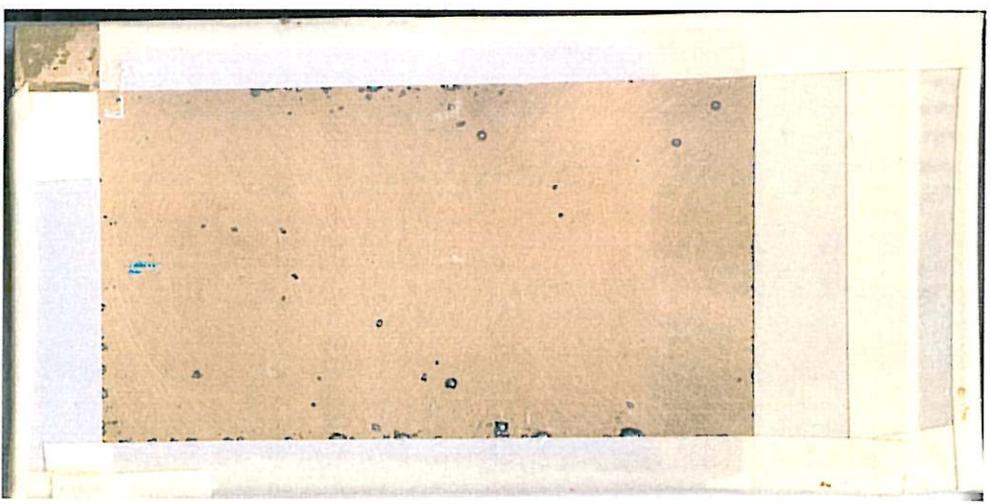


Figure 15. Images of representative panels
After 11 weeks of weathering.



**Polished Bronze
BTA + Incralac**



**Polished Bronze
FLC + A21**