

**FINAL REPORT TO THE  
NATIONAL CENTER FOR PRESERVATION TECHNOLOGY AND TRAINING  
1996 GRANT PROGRAM**

**1. Institution:** National Gallery of Art  
6th and Constitution Ave. NW  
Washington, DC 20565

**2. Project title:** RESEARCH INTO PROTECTIVE COATING SYSTEMS FOR  
OUTDOOR BRONZE SCULPTURE AND ORNAMENTATION

**3. Interagency Agreement Number:** NPS 14431A000195021

**4. Amendments to original Grant Agreement:**

As agreed, the project was suspended from mid March to the beginning of June 1996 while the principal investigator was away on maternity leave. Project dates were revised to reflect this suspension, including interim report, Sept. 30th, 1996, and final report, March 3 1,1997.

**5. Description of final grant product:** Final Report (see attached).

**6. Differences between planned and actual products of the grant:**

The main objective of investigating the performance of various protective coating systems, including standard coatings and new model coating systems, on outdoor bronzes has been addressed. Evaluation was based primarily on analysis of several physical properties of coatings on various substrates, including mean creepage from a scribe mark after weathering and overall visual assessment, plus chemical analyses of the coatings before weathering. Time delays caused by unforeseen events have limited the amount of weathering which could be achieved, however, so that physical and chemical analysis of the weathered coatings and coating/metal interfaces was postponed. Although this has limited the researchers' ability to draw conclusions about failure mechanisms involved in coating performance, the evidence gathered thus far raises important questions to be investigated in the future.

**7. Final Work-Cost Budget breakdown:**

Some expenditures forced budget reorganization as it pertains to funds granted by NCPTT to occur as follows:

A. Personnel:

Principal Investigator: Lynn B. Brostoff, Conservation Scientist,  
1/2 salary and fringe benefits: \$23,000

B. Equipment, including thickness gauge and adhesion equipment: 3,000

C. Supplies, including bronze substrates: 11,500

**D. TOTAL REQUESTED:** **\$37,500**

**8. Reasons for differences between the planned and actual work-costs:**

As indicated in the "Interim Report", the alloy of the first set of bronze which we commissioned was incorrect and the bronze samples had to be recast.

**9. Description of how this work advanced the field of historic preservation:**

The conservation community has expressed general dissatisfaction and frustration in numerous forums over current protective coatings used in the preservation of outdoor bronzes. As the deleterious effects of polluted urban environments on outdoor bronzes become increasingly evident, conservators and caretakers of bronze monuments are increasingly expressing the need for research into new coatings as a top priority. This research has laid the groundwork for insightful investigation into the problem of how coatings work and fail, and provides the basis for new, up-to-date information about coatings in use in the field and in industry. Future work, should it proceed, is expected to allow new recommendations concerning the conservation treatment of outdoor bronzes.

10. Planned Presentations and Publications: presentation scheduled for the Sculpture Conservation Workshop, Brookgreen Gardens, South Carolina, August 21-23, 1997; oral presentation at Eastern Analytical Symposium, Somerset, NJ, November 1997, possible presentation at Metal 98, ICOM-CC Metals Working Group conference, Draguignan, France, with subsequent publication, May 1998.

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**INTRODUCTION**

Outdoor bronze sculpture and ornamentation represent a significant part of our artistic and cultural heritage: bronze monuments number in the tens of thousands in this country alone. Increasing pollution in our environment, especially acid rain, has been linked to disfiguring corrosion of bronzes globally,<sup>1</sup> posing a serious threat to their aesthetic aspect and ultimate existence. In order to minimize the effects of outdoor atmospheric pollution on objects, it is necessary to use protective coatings. However, coatings in current use are often inadequate in their protective function.

Coating technologies currently used have been borrowed from traditional and industrial applications without accompanying research into adapting and optimizing materials and methods for conservation applications. These applications are generally distinguished from industrial applications by aesthetic considerations, and perhaps more importantly by physical and chemical differences. While industrial coatings are designed for fresh or primed metal surfaces, or stripped/blasted bare metal, surfaces of artworks and historical objects generally cannot be prepared in this fashion without unacceptable damage. Thus conservation applications typically require coatings to be applied onto inhomogeneous, corroded, and contaminated surfaces, which must retain their detail. Aesthetic criteria remain controversial, so that approaches to the appearance of outdoor bronzes after cleaning and coating continue to vary widely.<sup>2</sup>

Traditional coatings that continue to be popular for use on outdoor bronzes include: drying oils, such as lemon oil, paraffin oil, linseed oil and castor oil; pigmented, carnauba and beeswax mixtures; and commercial paste waxes.<sup>3</sup> These types of coating treatments greatly darken existing patinas and require frequent maintenance. Cellulose nitrate, which has poor outdoor durability, and Inctalac, an acrylic lacquer coating, are the most widely used modern coating materials on outdoor bronzes. Problems associated with Inctalac in normal application include insufficient thickness and physical defects such as orange peel, both of which appear to compromise the coating's effectiveness.<sup>4</sup> Other problems include pitting of the metal substrate, delamination and spalling, batch inconsistency, an often undesirable shiny appearance, and difficulty in removal. There has been at least one report of yellowing and crosslinking of Inctalac.<sup>5</sup> The relationship between these problems has not been investigated. Inctalac coatings also require relatively frequent maintenance, although less than the other coatings mentioned here.

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• <sup>1</sup>Andrew Lins and Tracy Power, "The Corrosion of Bronze Monuments in Polluted Urban Sites: A Report on the Stability of Copper Mineral Species at Different pH Levels," *Ancient and Historic Metals*, ed. D. A. Scott et al. (Getty Conservation Institute, 1994), pp. 119-151; T.E. Graedel, "The Corrosivity of the Atmosphere: Past, Present, and Future," *Dialogue/89 -- The Conservation of Bronze Sculpture in the Outdoor Environment*, ed. T. D. Weisser (NACE, 1992), pp. 13-32; Arthur Beale, "Conservation of Outdoor Sculpture: An Overview," *mid.*, pp. 3-12; Luc Robbiola and Christian Fiaud, "New Model of Outdoor Bronze Corrosion and Its Implications for Conservation," *Preprints, ICOM-CC 110th Triennial Meeting, Vol. II*, Washington, D.C., 1993, pp. 796-802.

<sup>2</sup> See, for example, Phoebe Dent Weil, "The Conservation of outdoor Bronze Sculpture: A Review of Modern Theory and Practice," *AIC Preprints, 8th Annual Meeting, San Francisco, CA, May 1980*, pp. 129-140.

<sup>3</sup> Copper Development Association (CDA), *Copper Brass Bronze Design Handbook: Architectural Applications* (New York, 1977), pp. 22-23.

<sup>4</sup>Intentional Copper Research Association, "Project 83: Development of an improved Inctalac," unpublished report.

<sup>5</sup> David Ehrhardt et al., "The Durability of Inctalac: Examination of a Ten Year Old Treatment," *Preprints, ICOM-CC 7th Triennial Meeting, Copenhagen, Sept. 10-14, 1984*, pp. 84.22.1-84.22.3.

The ultimate goal of the National Gallery's research project is to develop recommendations for better coatings and coating methods based on materials science testing methods and comprehension of mechanisms involved in coating failure. Short term objectives of the initial phase of the research, described below, include: evaluation of important physical aspects of the coatings in order to assess overall film quality after normal application; evaluation of a wide range of coatings that include new and traditional coatings, single and multi-part systems, based on accelerated weathering; and insight into the effect of different surface preparations and role of adhesion in the performance of coatings on two different types of "model" substrates, that is, on polished bronze and copper sulfate patinas. These results, along with limited chemical analyses, provide a basis for hypotheses concerning key factors in overall coating performance, as well as selection of coatings for future testing and evaluation.

## **EXPERIMENTAL**

Samples consist of 89 bronze ("Set I") and 89 copper roof coupons ("Set II") coated with 29 different coatings or coating systems, plus three controls of each type of substrate (totaling 180 samples). Both sets of samples are divided into three series of 30 each, which have undergone either a) no weathering, b) 1127 hr. accelerated weathering, or c) approximately 3 months outdoor weathering on the roof of the National Gallery of Art. In addition, several coupons of copper sheet with coatings, as well as glass slides with the basic coating types (see Table I), are included in the accelerated weathering tests.

The bronze substrates were investment wax cast with a "plaque alloy" in pairs, each measuring 15" x 6" x 1/8", and polished to a mirror finish by Art Research and Technologies, Inc. The copper roof samples were generously donated by the Architect of the Capitol. They were obtained from the Library of Congress in Washington, DC, where the roof is undergoing replacement. The copper sheets had been exposed at an incline of about 30 degrees, due south, for approximately 50 years. Several adjacent sheets were sheared into 5" x 6" coupons. The coupons chosen for coating have a fairly even, light green patina with black spots which are either finely distributed or large and raised, there are also light yellow-orange spots on many samples.

### Surface preparations and spray coating

A list of coatings used in the study is shown below in Table I.

**TABLE 1**

DESCRIPTION	MAIN INGREDIENT	BTA pretreat-ment	SILANE pretreat. ment	WAX top coat
1. *Incalac (StanChem, Inc.)	Acryloid B-44 (Rohm & Haas)			
2. BTA pt + Incralac (BTA=benzotriazole)	Acryloid B-44	√		
3. Incralac + wax	Acryloid B-44			√
4. BTA Pt + Incralac + wax	Acryloid B-44	√		√
5. Incralac w/ 2% Tinuvin 292	Acryloid B-44			
6. Incralac w/ silane (2% γAPS)	Acryloid B-44			
7. silane Pt + Incralac	Acryloid B-44		√	
8. thick Incralac (5 coats)	Acryloid B-44			
9 *B-48	Acryloid B-48 (Rohm & Haas)			
10. *CCR acrylic (CCR=Cape Cod Research, Inc.)	Acryloid B-48			
11. silane pt + CCR acrylic	Acryloid B-48		√	
12. *NK 11565 (NK=J.G. Nikolas & Co., Inc.)	(Acryloid B-48)			
13. *PPG DCA468 (PPG=PPG Industries, Inc.)	acrylic lacquer			
14. PPG DCA468 + DAU75	acrylic lacquer/urethane			
15. NK 11565 +NK 9778	acrylic lacquer/urethane			
16. BTA pt +NK 11565 +NK 9778	acrylic lacquer/urethane	√		
17. silane pt+NK 11565 +NK 9778	acrylic lacquer/urethane		√	
18. NK 11565 + NK 9778 + wax	acrylic lacquer/urethane			√
19. *NK 9778	acrylic urethane			
20. *PPG DAU75	acrylic urethane			
21. manufacturer's pt + PPG DAU75	acrylic urethane			
22. silane pt + NK 9778	acrylic urethane		√	
23. *CCR silicone alkyd (brushed)	silicone alkyd resin			
24. *CCR polyurethane (brushed)	2-part wb polyurethane			
25. silane pt	γ APS silane (OSi Industries)		√	
26. *StanChem "wb Incralac"	wb acrylic urethane			
27. *NK 11650	wb acrylic urethane			
28. *Veloz wax (spayed)	synthetic wax mixture			
29. BTA pt +Veloz wax (sprayed)	synthetic wax mixture	√		
30. control				

for\_sample\_Set II\_only:

31. BTA pt + CCR acrylic	Acryloid B-48	√		
32. silane pt + CCR polyurethane	polyurethane		√	
33. BTA pt	benzotriazole	√		
34. control				

pt = pretreatment; wb = waterborne; basic coating type

Surface preparations may be summarized as follows. The bronze samples were solvent cleaned by immersion, wiping, and rinsing in a series of solvents of different polarity in order to remove fatty polishing residues on the surface and in the pores, and to generally reduce surface tension for better wetting of the coatings. Selected samples also underwent the following, as indicated above: a) immersion in 1.5% BTA/ethanol, a corrosion inhibitor, b) brushing a 2% solution of aminopropyltriethoxysilane (7APS), a coupling agent, in propanol/water, or c) the PPG (manufacturer's recommended) pretreatment: light etch cleaning with a phosphoric acid/chromic acid solution. The purpose of the latter treatment is to expose a

new metal surface and possibly to create a thin passivating film to inhibit corrosion and promote good adhesion. Copper roof samples were cleaned with light scrubbing in deionized water and Triton X-100, a non-ionic surfactant, and air dried. Subsequent pretreatments were as for bronze (see Table I).

Most coatings were spray-coated, following manufacturers' recommendations as closely as possible, by Andrew Baxter of Bronze et al., an experienced practitioner of spray coatings. Several samples were brush-coated as noted in Table I. The Veloz wax coatings were applied by Nikolas Veloz using a spraying and reheating technique. Top coat waxing, using the Veloz wax mixture, was applied cold by brushing and buffing. After coating, the bronze plaques were cut on a bandsaw into three equal pieces to the new dimensions of 5" x 6" coupons. Series B and C of each set are scribed with a 2" vertical line in the bottom middle of the sample and edges of these panels were waxed. All samples have been photodocumented in their before-weathering state and stored in the dark in polyethylene bags in a controlled environmental room at 23 °C and 50% RH when not otherwise undergoing weathering (see attached photographs of controls).

### Weathering

The initial accelerated weathering program, which may be called a "modified Volvo test," consisted of a) exposure to light (outdoor simulation) and dark cycles with humidity and temperature cycling in an Atlas Ci65a xenon-arc weatherometer, and b) exposure to humidity and freeze-thaw temperature cycling with "acid rain" spraying twice per week in a Tenney Thirty temperature/humidity test chamber. The programs are shown schematically in Figures 1 and 2. The spray solution consisted of a 1:1 mixture of 1% NaCl and H<sub>2</sub>SO<sub>4</sub>/HNO<sub>3</sub> "acid rain" solution, and the final solution pH was 4.0 (adjusted with the addition of NaOH). The concentrations of SO<sub>4</sub> and NO<sub>3</sub> in the mixture were 440.6 and 344.4 meq/l, respectively. Accelerated weathering conditions for a second run (currently underway) have been modified to better conform with ASTM G26 standards; modifications include a higher irradiance level, more cycling with the elimination of conditioning cycles, and "acid rain" spraying five times per week. The "acid rain solution" has also been altered, based on experimental work of Nassau et al.<sup>6</sup> Total sulfate and nitrate concentration in the new solution are reduced to 60.0 and 22.0 meq/l, respectively, and chloride and sodium concentrations are reduced to 10.0 and 18.7 meq/l, respectively. The solution pH is 3.0. For outdoor weathering of the samples, painted wood racks have been constructed and positioned on the roof of the National Gallery of Art, West Building, so that samples are exposed due south at a 45° angle according to ASTM G7.

### Methods of evaluation

Metal substrates were analyzed by secondary emission energy dispersive X-ray fluorescence spectroscopy (XRF) using a Kevex 0750A spectrometer equipped with a BaCl<sub>2</sub> secondary target and 6 mm collimators. The anode voltage and current were 60 kV and 0.4 mA, respectively. Live accumulation time was 200 seconds. Elemental weight percentages were calculated with EXACT (energy dispersive X ray analysis computation technique), a software program provided by Kevex. Metal substrates were also characterized by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) using a JEOL 6300 scanning electron microscope equipped with a Link Super ATW Si(Li) detector and a Link eXL II spectrometer. The accelerating voltage was 10-20 kV, depending on the sample. Selected corrosion products were analyzed by powder X-ray diffraction (XRD) using a Philips X-ray generator 3100 equipped with a copper target and nickel filter to provide Cu K $\alpha$  radiation, 45 kV anode voltage, and 25 mA current.

Coatings and the copper roof patina were analyzed by Fourier-transform infrared spectrometry (FTIR), and coating/metal interfaces were selectively analyzed by reflection-absorption infrared

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<sup>6</sup>K Nassau et al., "The Reaction of Simulated Rain with Copper, Copper Patina, and some Copper Compounds," Corrosion Science Vol. 27, No. 7(1987), pp. 703-71.

spectroscopy (RAIR) and/or attenuated total reflectance spectroscopy (ATR), using a Bio-Rad FTS-60A spectrometer equipped with an external UMA 300A microscope and appropriate accessories. Coatings were also analyzed by pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) using a CDS 2000 Pyroprobe mounted directly onto the injector of a Varian 3500 capillary gas chromatograph equipped with a RTX-1 column (32mm ID, 30 m, .25 microns film thickness) and interfaced to a Finnigan 800 Ion Trap Detector (ITD). Pyrolysis was carried out at 600 °C for 10 sec; the Py-GC interface was held at 300 °C, the GC oven was programmed with an initial temperature of 40 °C (held for 5 mm.) and increased to 300°C (held for 10 mm.) at a rate of 8 °C/min. The column was interfaced directly to the ITD; the transfer line was at 250°C. The scan range was 35-550 amu, scan time 1 sec, and data analysis was with Finnigan ITD

4.10. The split/splitless injector was at 300 °C in the split mode, with a split ratio of about 100:1; the carrier gas was helium.

Dry film thickness of coatings before weathering (ASTM D1400) was determined using an Elcometer 345 dry film thickness gauge (eddy current method) directly on the samples. Between 50 and 70 readings were taken on each sample. The bronze coating measurements were subject to an error of about 5%; the copper roof samples had a large margin of error which could not be determined due to the rough and uneven patina. Samples were also examined under magnification for assessment of overall film quality, including the presence of orange peel, air entrapment, solvent popping, pinholing, bumps and sinks, cratering, and crawling and dewetting.

Coating adhesion was evaluated by the cross-cut adhesion/tape test (ASTM D3359). In this method cross-hatch cuts or X's are cut through the coating with a specified tool. A piece of tape is then pressed onto the cuts and pulled off, and the remaining coating is rated on scale of 0-5 for adhesion. (For graphing purposes, de-adhesion is shown in some figures by inverting the ratings so that 0=best.) This test produces a rough estimate of adhesion, and is capable of differentiating adhesion between coatings. The method does not, however, distinguish between types of adhesive failure, including cohesive and interlamellar failure in multi-part coating systems, and results were therefore somewhat deceptive in these cases. Tensile adhesion testing using a portable tester was attempted but was found to be too inaccurate and insensitive to produce meaningful results.

Series B and C samples were evaluated visually after initial weathering for overall % area corrosion (ASTM D610) and for corrosion creepage at a two inch vertical scribe marked at the bottom of each sample (ASTM 1654). Mean creepage was calculated based on measurements made under 40x magnification approximately every 1/8" along each side of the scribe mark, resulting in 20-26 measurements per sample. No blistering or checking of the coatings was noted.

## **RESULTS AND DISCUSSION**

### Substrate characterization

XRF analysis confirmed that the bronze alloy composition (% weight) is about 87 Cu, Sn 5, Pb 2, Zn 4, with a small nickel contaminant (about 0.6%). SEM imaging of the bronze surface revealed numerous pits as well as random groupings of dark spots (Figure 3a). EDS analysis of the pits showed the presence of aluminum and oxygen, most likely from grinding compounds and/or oxidation products. EDS of the dark spots showed the presence of carbon, but not in the surrounding areas, indicating that the spots are most likely from fatty polishing residue. SEM backscattered imaging clearly reveals the metal microstructure: it consists of a three-phase dendritic structure, containing a Cu-Sn-Zn and a similar Sn-rich Cu-Sn-Zn phase, in addition to isolated globules of Pb, which are fairly evenly spread throughout (Figure 3b).

XRF analysis of the copper sheet indicated that the copper has a purity of 99.93%. XRD analysis of the patina provided positive identification of the following crystalline phases: copper, cuprite ( $\text{Cu}_2\text{O}$ ), brochantite-O (orthorhombic and monoclinic mixture) ( $\text{Cu}_4\text{SO}_4(\text{OH})_6$ ), antlerite (minor;  $\text{Cu}_3\text{SO}_4(\text{OH})_4$ ), and possibly copper sulfide. Some unidentified weak lines remained in the XRD pattern; no tenorite ( $\text{CuO}$ ) or copper chlorides were detected. The black spots were shown to have an identical pattern to the general green patina, containing only cuprite, brochantite, and copper sulfide, with only one, faint new line at  $d=3.32$ . This was not identified. The Fourier-transform infrared (IR) spectrum of the patina (Figure 4) shows excellent agreement with the spectrum of pure brochantite<sup>7</sup>. No differences were detected in the IR spectra of green and black patina components.

SEM imaging of the copper roof patina shows a very rough and porous morphology (Figure 5a). EDS analysis of the green patina revealed the presence of Al, Si, Fe and P contaminants in addition to Cu, S, and O. The presence of phosphorous in outdoor bronze and copper patinas has been sporadically noted, particularly in connection with black spots on copper patinas, and has been variously attributed to airborne fertilizer-containing particles or pigeon droppings<sup>8</sup>. The other contaminants are commonly found in airborne dirt particles. No carbon was detected. (Nitrogen cannot be detected from this detector array.) Most interestingly, SEM/EDS analysis of black spots in the patina revealed the presence of Cl, Ca, and V, the latter of which there is no explanation at present (Figure 5b). The presence of silicon as well as aluminium also appeared relatively higher in this spot.

#### Chemical characterization of the coatings

Chemical characterization of most coatings included analysis by IR and Py-GC/MS. Results are included in the discussion below. Samples #1-8 have coatings based on Inralac. This coating was developed by the International Copper Research Association (INCRA) in 1964. It is an unpatented formulation made from Acryloid B-44, a thermoplastic methyl methacrylate copolymer manufactured by Rohm and Hans; the corrosion inhibitor benzotriazole (BTA) (often referred to as a chelating agent); and a leveling agent, either Paraplex G-60, an epoxidized soybean oil, or a silicone oil. The sole manufacturer of Inralac in the United States at present is StanChem, Inc., in East Berlin, CT. Their literature states that Inralac is formulated from “a blend of acrylic resins,” and also contains “a U.V. absorber and a chelating agent.” This manufacturer claims that they are producing Inralac according to the original formulation, using a silicone oil and adding a UV absorber.

Py-GC/MS analysis of Inralac identified the major fraction as methyl methacrylate, as expected. There were also two smaller fractions that were identified as ethyl acrylate and ethyl methacrylate, both of which were also identified in B-44. In addition, a very small fraction of butyl methacrylate, which was not found in the sample of B-44 analyzed here, was identified. Py-GC/MS also revealed the continued presence of solvent molecules in films of both B-44 and Inralac which were applied to glass slides about one year prior to analysis. The IR spectrum of Inralac is shown in Figure 6a. Compared with B-44 (not shown), the peak near  $1729\text{ cm}^{-1}$  shows a much wider distribution of carbonyl absorptions, including additional weak absorptions near  $1689$  and  $1616\text{ cm}^{-1}$ . This suggests the presence of a small portion of carboxylic acid functionalities in the polymer. Methacrylic acid is commonly copolymerized with other polymers in order to enhance adhesive properties. Examination of a copper sheet with a thin coating of Inralac by RAIR, along with examination by ATR of the fracture surface of a flake of Inralac delaminated from copper (Figure 7), shows that the wide carbonyl vibration seen in the bulk spectrum is

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<sup>7</sup>K. Nassau et al., “The Characterization of Patina Components by X-ray Diffraction amid Evolved Gas Analysis,” Corrosion Science Vol. 27, No. 7(1987), pp. 669-684.

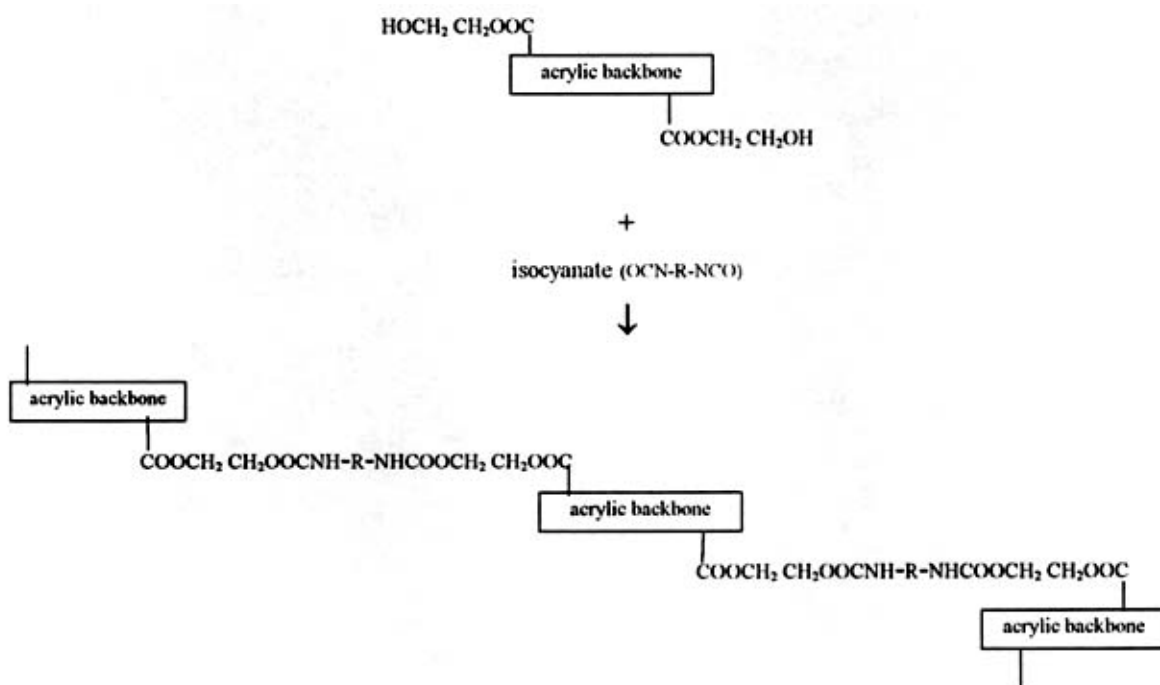
<sup>8</sup>T.E. Graedel et al., “Copper Patinas Formed in the Atmosphere-I,” Corrosion Science Vol. 27, No. 7 (1987), pp. 639-657; L.S. Selwyn et al., “Outdoor Bronze Statues: Analysis of Metal and Surface Samples,” Studies in Conservation 41(1996), pp. 205-228..



split into at least two separate peaks on the copper sheet, and is comprised of one sharp peak on the coating side of the coating/metal interface. This provides evidence for selectivity and orientation of carbonyl groups at the metal interface and points to a chemical bonding component of the adhesion between Incralac and copper alloy substrates. Further investigation by IR, Py-GC/MS and gel permeation chromatography (GPC) analysis should elucidate the structure of these acrylic copolymers and their interaction with copper alloy surfaces.

Acryloid B-48 is a higher molecular weight methyl methacrylate copolymer manufactured by Rohm and Hans, with reportedly better adhesion to metals and, in particular, to untreated metals. It is unknown how this copolymer is modified in comparison to B-44 other than in terms of molecular weight. The manufacturer's literature shows that B-48 is more flexible than B-44, and recommends that it be used instead of B-44 in the Incralac formulation. Py-GC/MS analysis of this resin showed differences with that of Incralac and B-44. Three large components were detected; these were identified as methyl methacrylate, butyl acrylate, and butyl methacrylate. There were also two unidentified components. The JR spectrum of B-48, shown in Figure 6b, is similar to that of Incralac, except in the relatively higher proportion of methylene functionalities, the interesting absence of peaks near  $1689$  and  $1616\text{ cm}^{-1}$ , the additional presence of a peak at  $1080\text{ cm}^{-1}$  which may be tentatively attributed to a primary alcohol vibration, and what appear to be weak, broad absorbances centered around  $3300\text{ cm}^{-1}$  which are also attributable to OH vibrations. The latter two features suggest the presence of a small fraction of hydroxyl functionalities. The composition of B-48 should be investigated further. Other commercial thermoplastic acrylic coatings in this study include a) a Cape Cod Research (CCR) acrylic coating formulated from B-48, b) PPG Industries' DCA468, the JR spectrum and Py-GC/MS analysis of which indicate it is probably formulated from B-48 or a similar resin, and c) G.J. Nikolas & Co., Inc. (NK) 11565, which shows a near perfect match by JR with B-48.

Thermoset acrylic urethane coatings in the study include two basic varieties: solvent-borne, 2-part systems, and 1-part waterborne systems. The solvent-borne coatings are based on acrylic polyols (or hydroxyl functional acrylics) which are reacted with an aliphatic di-isocyanate crosslinking agent according to a general scheme similar to the following:



Catalysts, flow aids such as silicones, UV stabilizers, and defoamers are typically added to these coatings. The IR spectrum of PPG DAU75 (Figure 8a) is characterized by a small, broad, double absorption near  $3520\text{ cm}^{-1}$ , aromatic vibrations near  $3026$ ,  $1602$ , and  $1500\text{ cm}^{-1}$ , and a sharp carbonyl vibration near  $1732\text{ cm}^{-1}$ . Py-GC/MS showed evidence for a styrene/methyl methacrylate/butyl methacrylate terpolymer (along with unidentified components), indicating that the aromatic groups in the IR spectrum may be attributed to polystyrene.

ATR of the PPG acrylic urethane coating (coating/metal interface) after delamination from a bronze coupon (Figure 9b) shows a dramatic difference from the IR spectrum of the bulk polymer (Figure 9a). The ATR spectrum shows that urethane functionalities, identified by new peaks in this spectrum near  $1526$ ,  $1691$ , and  $3390\text{ cm}^{-1}$ , are concentrated at the metal interface. In addition, a weak peak at  $2232\text{ cm}^{-1}$  indicates the presence of unreacted isocyanate at the metal surface. These results suggest preferential adsorption and/or direct chemical interaction of urethane and isocyanate groups at metal surface, which would correspond to differences in crosslink density and chemical composition of the coating at the interface.

The Nikolas 9778 acrylic urethane is an acrylic polyol/di-isocyanate system which appears from infrared analysis to contain a polystyrene component. The IR bulk spectrum (Figure 8b) also shows a much higher relative proportion of NH and NCO vibrations (from the urethane linkage) near  $3393$  and  $1519\text{ cm}^{-1}$  respectively than seen in the bulk spectrum of DAU75. This indicates a much greater crosslink density in the bulk coating, and would greatly affect its properties. An experimental set of acrylic/acrylic urethane multi-part coating systems using the Nikolas coatings were included in the study. The purpose of these coatings was to combine the good adhesion characteristic of one coating with the expected superior outdoor durability of the other, as well as to present an excellent and unique method for coating removal consisting of solvent “peeling.”

IR analysis of the StanChem waterborne acrylic urethane (not shown) revealed the presence of unreacted isocyanate, plus a larger relative amount of phenyl vibrations compared to the solvent-borne acrylic urethanes. IR analysis of the NK 11560 waterborne acrylic urethane showed a relatively small proportion of phenyl vibrations and a relatively large proportion of NH/OH vibrations.

The two-part waterborne polyurethane (CCR) is a polyurethane polyol dispersion in water, mixed with a commercial crosslinking agent and blended with various organic corrosion inhibitors and UV absorbers. The CCR silicone alkyd coating is made by condensation co-polymerization of a silicone resin and an organic resin and blended with various organic corrosion inhibitors and UV absorber. CCR coating formulations are known, as part of a secrecy agreement with CCR.

The Veloz wax coating is a blend of about 75% Bareco Victory Wax (microcrystalline, synthetic, low melting point wax), plus Bareco Polywax 2000 and 500 (polyethylene microcrystalline waxes), and Petronauba C, an oxidized polyethylene wax.

### Physical properties of coatings

The quality and aesthetics of the coatings varied not only between coatings but on the two different substrates (see photographs, attached). On the polished bronze substrate, most coatings appeared aesthetically appropriate, with two exceptions. The thickly sprayed wax coatings appeared matte, opaque looking and uneven; under magnification “grains” could be seen that often showed gaps. The silicone alkyd was thick and orange-brown in color before application. CCR stated that this batch may have been unstable. In addition, coatings which resulted in poor film quality on bronze included, notably: thick Inralac, which developed severe orange peel; the StanChem waterborne acrylic urethane, which developed dense pinholing in the second coat; and the brushed coatings, which were streaky, uneven, and full of

solvent popping. Other coatings which had fairly dense pinholing and/or solvent/air popping included Incralac coatings and the CCR acrylic coatings. Coatings which developed light orange peel or other texture included: Incralac with silane formulation, BTA pretreatment plus Incralac, and silane pretreatment plus NK acrylic/acrylic urethane. Silane pretreatment produced a slight streakiness on bronze, which was attributed to its application in too concentrated a form. BTA and the PPG recommended pretreatments were invisible.

The quality and aesthetics of coatings on the copper roof samples were much more varied, especially with regard to color effect, and generally resulted in poor aesthetic results. An unchanged appearance was very difficult to achieve on the mineralized surfaces: only B-48 and the NK waterborne acrylic urethane boasted this achievement. Incralac appeared dark, shiny and produced welling and pooling around surface imperfections. The other acrylics went on somewhat more evenly. The urethanes appeared very shiny and saturated, resulting in a dark, muddy green color. Top coat waxing generally improved appearances. It should be noted that matting agents are available for use with the acrylics and acrylic urethanes, which would help minimize their shininess. The effect of matting agents was not addressed in this study, and therefore were not included. The pure wax coatings were dark, matte, muddy and uneven-looking. Under magnification, gaps could be seen between “grains” of cooled wax. Coating quality on the copper roof samples was similar to that on bronze but was masked by the patinated surface. In particular, it was noted that the Incralac and B-48 coatings had peculiar wetting properties on the patinated surface, and produced a microscopic “shrink-wrap” appearance upon drying. Silane pretreatment, as well as the BTA and the PPG recommended pretreatments, were invisible on the copper roof panels.

Results of dry film mean thickness on the two substrates are shown together with the standard deviation on bronze in Figure 10. Results of adhesion testing before weathering are shown in Figure 11. In general, results show that initial adhesion of coatings on copper roof panels is equal to or better than that on bronze for most samples, with a few exceptions. This may be attributed mainly to increased mechanical adhesion on the rough surface and penetration of coatings into the mineral layer. The latter is demonstrated in Figure 10 by the measured differences between bronze and copper roof coating film thickness as compared to the thickness of the patinated control. This is shown to be an important factor, for instance, in the case of the NK waterborne acrylic urethane, in which very little patina penetration occurred and very poor adhesion was measured on the copper roof panels, but not on bronze. It was noted that this coating looked very good on the copper roof samples, with almost no perceivable change to the appearance of the substrate. In this case, good appearance appeared to come at the expense of adhesion.

Additional coatings which showed poor adhesion to both types of substrates included the CCR polyurethane and the StanChem waterborne acrylic urethane. The lack of good adhesion between substrates and all three waterborne coatings suggests that a surface tension effect may have been involved. The PPG acrylic and acrylic urethane showed very poor adhesion to bronze without any pretreatments, but fairly good adhesion to the copper patinas. B-48 and the silicone alkyd showed excellent adhesion to both types of substrates. Results also show that the silane pretreatment dramatically improved adhesion of Incralac and the CCR acrylic to bronze, but had no apparent effect on the copper roof panels. The effect of silane pretreatment could not be properly assessed by the cross-cut adhesion test on multi-component systems, which had mixed interlamellar and whole system failure. The PPG manufacturer’s pretreatment also dramatically improved adhesion of the PPG acrylic urethane to bronze, but not to the copper roof samples. BTA showed no detectable effect on adhesion by this test method. Future work should include adhesion testing of samples after weathering, as well as another method of adhesion testing if possible.

Other physical data, such as air and water vapor permeability and coating flexibility, was not found in the literature in a form which would enable correlation or comparisons. These properties should be investigated for individual coatings in the future. As previously mentioned, Incralac and other acrylic lacquers produced a “shrink-wrap” appearance upon drying on patinated surface vs. the more leveled films

of other types of coatings. This points out the importance of collecting surface tension data for the coatings and substrates, such as by contact angle measurements. This should be undertaken in the future for select coatings.

#### Evaluation of samples after initial weathering: general observations

Comparison of coating performance on the cast bronze and copper roof panels after initial accelerated weathering is shown in Figure 12, and comparison of coating performance on these substrates after initial outdoor weathering is shown in Figure 13. Figure 14 shows the performance rating of coatings on bronze after accelerated weathering together with dry film mean thickness and adhesion data.

Series B and C samples were examined after initial weathering for overall signs of corrosion and coating failure (ASTM D610 and D714), and for corrosion at a two inch vertical scribe marked at the bottom of each sample (ASTM 1654). Relatively few samples showed signs of overall corrosion and/or general coating failure. One notable exception was the StanChem waterborne acrylic urethane, which showed marked yellowing and embrittlement after both accelerated and outdoor weathering. Visual examination of the samples revealed different amounts of corrosion in the scribes themselves. Some samples appeared to be almost protected from corrosion in the exposed scribe, while others appeared to have accelerated corrosion in the scribe, probably as a result of localized electrochemical differences created by coated and uncoated areas. This should be investigated further. In the case of outdoor sculpture, a cathodic-type protection would offer an important advantage, since coatings are not only subject to imperfections such as pinholes when applied, but scratches and other wear may result during the lifetime of the coating. Coating condition and corrosion in the scribes were noted but not included in performance ratings since it is not clear at present how these factors should be weighted in overall coating performance.

Other than by examination of the scribes, the copper roof samples were generally difficult to evaluate since new corrosion was often difficult to distinguish from the pre-existing patina. Results for these samples after initial weathering are thus more variable and somewhat less reliable. However, it appeared that the bronze samples experienced relatively more corrosion phenomena from exposure to both accelerated and outdoor weathering. This is to be expected from a polished, cast surface versus an already corroded surface, but also appears to correspond in most cases to the generally poorer adhesion of coatings to the polished bronze substrates. For example, samples #14 and 20, PPG acrylic/acrylic urethane and PPG acrylic urethane alone, showed large differences in adhesion and coating performance on bronze and copper roof after both accelerated and outdoor weathering (see Figures 11, 12 and 14).

The corrosion initiated in accelerated and outdoor weathering on the various samples was often quite different in appearance. Accelerated weathering in particular produced various corrosion patterns and colors at scribes, indicating that corrosion mechanisms may vary in association with different coatings. On bronze, most areas of corrosion appeared to begin with thin films of orange-red-brown cuprite formation, often etched in appearance, followed by accumulation of light green and sometimes black spots on top of the red, as well as isolated thick green crusted areas. Samples pretreated with silanes or containing silanes in the formulation showed brown or gold spots radiating out from the scribes. Samples were also water-spotted. On bronze exposed outdoors, orange-brown areas appeared etched and often speckled with light green; green, red, and black corrosion. Some type of biological attack was also noted on these samples in the form of filaments which were easily wiped off, and samples generally were covered with dirt, particularly the waxed coatings. The samples treated only with silane appeared similar after both indoor and outdoor weathering, with variegated areas of matte brown-orange and shiny gold metal.

Copper roof panels exposed to accelerated weathering often exhibited blackish corrosion in the scribes and under intact coatings near the scribes. This was not noted on samples exposed outdoors. New light green corrosion, as well as white accretions, were also noted in the scribes of samples after accelerated

weathering. The control and samples treated only with silane or BTA showed areas of dark green toward the bottom and around edges where more wetting took place. As expected, samples exposed outdoors did not exhibit much change: scribes most often appeared orange-brown, presumably from cuprite formation, with some new light green corrosion visible to various degrees. The waterborne acrylic urethane coatings after both types of weathering were unique in the appearance of a tide-line of corrosion outside the scribe, apparently from water penetration and spreading under the coatings.

### Initial accelerated weathering results

XRD results for corrosion scraped from selected samples after accelerated weathering are shown in Table II, below:

**TABLE II**

SAMPLE	COLOR(S)	PHASES IDENTIFIED	UNIDENTIFIED LINES
30B, control bronze	orange-brown green	<ul style="list-style-type: none"> <li>• cuprite</li> <li>• paratacamite</li> <li>• other copper chloride hydroxides, including atacamite and botallackite</li> <li>• CuCl</li> <li>• brochantite (minor)</li> <li>• zincian chloride hydroxide (?)</li> </ul>	
30B, control copper roof	dark green black orange-red	<ul style="list-style-type: none"> <li>• only new lines compared to before weathering samples identified as paratacamite</li> </ul>	
1B. Inralac on bronze	powdery, light green	<ul style="list-style-type: none"> <li>• cuprite</li> <li>• paratacamite</li> <li>• botallackite</li> <li>• NaCl</li> </ul>	d4. 16 (weak)
1B. Inralac on copper roof	green	<ul style="list-style-type: none"> <li>• cuprite</li> <li>• paratacamite/ atacamite</li> <li>• NaCl</li> </ul>	d=4. 14 (strong) d=3.75 (strong)
15B, NK acrylic/acrylic urethane on copper roof	green/greenish-black red	<ul style="list-style-type: none"> <li>• cuprite</li> <li>• paratacamite + other copper hydroxy chlorides</li> </ul>	d=4.71 d=3.42

These results show that corrosion products occurring from accelerated weathering consisted mainly of cuprite and paratacamite, a basic copper trihydroxy chloride ( $\text{Cu}_2(\text{OH})_3\text{Cl}$ ). Paratacamite is listed in JCPDS International X-ray Diffraction Files as greenish-black as well as light green, and this is most likely the identity of the new black corrosion formed on copper roof panels during accelerated weathering. The identity of new black corrosion on the outdoor bronze samples is not clear, however. It is possible that cuprite at a certain thickness has a black interference color. This question should be investigated further. Unidentified lines in the patterns from substrates coated with acrylics suggest the presence of additional products which may be related to the individual coatings and its additives. This subject should be further investigated by both JR and XRD. It is clear from XRD results, however, that the accelerated weathering regime did not realistically represent the copper sulfate and sulfide corrosion mechanisms which

predominate in typical outdoor environments. This was attributed to too much NaCl in the rain solution.

Comparison of performance ratings for the coatings on bronze and copper roof panels after initial accelerated weathering is shown in Figure 12. The samples treated only with silane were omitted from this and the outdoor evaluation since the film did not appear to act as a coherent protective coating. Silane treated samples should undergo further chemical analysis. The overall performance ratings were calculated by addition of millimeters of mean creepage of corrosion from the scribemark to a normalized factor of estimated % area corrosion. Ratings are shown to be quite different for the two types of substrates. This is due in part to the difficulty in assessing corrosion outside the scribemark on the copper roof samples, as indicated above. However, the general lack of correlation between coating ratings on the two types of substrates appears to arise from true differences in performance.

On bronze, acrylic/urethane systems clearly outperformed other coatings. This appears to be partly due to a thickness factor as well as the inherent protective capability of the acrylic urethane. Next in performance on bronze was the Incralac series, which had intermediate thickness and adhesion, followed by the NK acrylic urethane. The Veloz wax coatings and B-48 performed worst, in the latter case at least partly due to the thinness of the coating. Permeability may have been a factor in both of these cases. Performance problems appeared also with the Incralac + Tinuvin 292 formulation and the CCR acrylics, the latter of which were applied rather thinly on bronze and contained many film flaws.

Coatings which performed noticeably better on copper roof than on bronze include the wax and waxed coatings, CCR polyurethane, and Incralac with Tinuvin 292 formulation. The high ratings of the wax coatings on copper roof panels are partly attributable to spreading of wax in the scribe during cutting. In a sense, the wax and waxed coatings were "self-healing." It is not clear, however, why this effect was not as marked on bronze. Coatings which performed somewhat better on copper roof panels than on bronze include both PPG acrylic urethane coatings, B-48, silane pretreatment + Incralac, and the silicone alkyd. NK acrylic/acrylic urethane systems did not perform as well on copper roof panels as on bronze. Both waterborne acrylic urethanes performed worse on copper roof panels than on bronze, although they did not perform very well on bronze either.

Results generally do not show an obvious benefit from BTA pretreatment on either substrate outside of experimental error range, except in the case of the Veloz wax coating, which did not contain BTA in the formulation. There is also a question, however, whether the BTA treatment took properly to the bronze substrates, since oil and fat residues were found to be very difficult to remove. The presence of BTA on a treated copper roof panel was confirmed by EDS analysis; similar analysis of a bronze coupon treated with BTA was inconclusive. In general, however, results so far appear to support the usefulness of BTA as an additive in coatings.

The effect of the silane on various coating systems was difficult to assess since this silane is very reactive and will affect adhesion as well as chemical changes such as crosslinking and yellowing in coatings. Results show that Incralac with silane pretreatment performed significantly more poorly than other coatings, although it was thinner. On the other hand, Incralac with silane added in the formulation did somewhat better than the plain Incralac coating. Silane pretreatment with NK acrylic urethane appeared to have helped performance on bronze. The effect of silanes needs to be clarified with further investigation. For practical applications, a less reactive silane should be chosen for future work.

### Initial outdoor weathering results

As expected, the samples exposed outdoors exhibited less corrosion than those exposed to accelerated weathering. The majority of bronze samples from series C showed the formation of orange-red cuprite with black areas interspersed in the scribes, along with brown-green dendritic corrosion in areas which lost coating, were uncoated, or were under pure wax coatings. As mentioned, copper roof samples

showed little change except for corrosion in the scribes. The samples were evaluated visually on a scale of 0-5 in order to roughly assess relative performance at this early stage of outdoor exposure. In addition, it should be noted that a group of samples blew over and were upside down for an undetermined period of time, which probably affected the results. However, this is not expected to affect results significantly after a long period of exposure outdoors. For these reasons, no firm conclusions can be drawn from the outdoor exposure at present. However, several observations based on initial results, shown in Figure 13, are possible.

The best performers on both types of substrates after preliminary outdoor exposure include some of the Incralac coatings, followed by most of the NK acrylic/acrylic urethane coatings and the silicone alkyd coating. On bronze, samples #5 and #6, the two Incralac coatings into which additives were mixed, plus the thick Incralac, performed markedly worse than other Incralac coatings. BTA and silane pretreatments on bronze generally appear to have improved coating performance, except in the case of pure wax (which performed very poorly) and the NK acrylic and acrylic urethanes. In contrast, no improvement from either BTA or silane pretreatment is seen so far on the copper roof panels. The manufacturer's pretreatment for the PPG acrylic urethane gave a marked improvement in the performance of this coating on bronze, but the coating fared worse after pretreatment on the copper roof panel. Copper roof panels with pure wax or wax top coats received the highest ratings after outdoor exposure, as with accelerated weathering. Again it was apparent that wax got into the scribes and acted almost as "self-healing." It is not clear, however, whether the large difference in performance of pure wax coatings on bronze and copper roof panels is real or due to difficulty in assessing the condition of copper roof panels after the short exposure. It is expected that results will be clearer after additional weathering.

## CONCLUSIONS

This one year study has revealed important questions, including how different factors should be weighted in overall coating performance and why there may be marked differences in coating performance on different types of substrates. Results after weathering of bronze and copper roof samples to date do not show dominant trends which correlate performance and any one property such as thickness or adhesion (see Figure 14). Although it was predicted that adhesion should have rough correlation to performance, this has not been borne out so far. This may be due in part to a time factor, as well as to observed divergence in corrosion mechanisms in accelerated weathering caused by exposure to NaCl. Results do suggest partial correlations, as discussed above, but also highlight exceptions that cannot be explained by coating thickness or adhesion. This was the case, for example, with the mediocre performance of PPG acrylic urethane after manufacturer's pretreatment, despite excellent adhesion, adequate thickness, and good overall film quality. Results thus point to coating performance as a complex puzzle of interdependent factors, including coating thickness, water and oxygen permeability (related to thickness), adhesion and wetting (related), flexibility, and coating film quality.

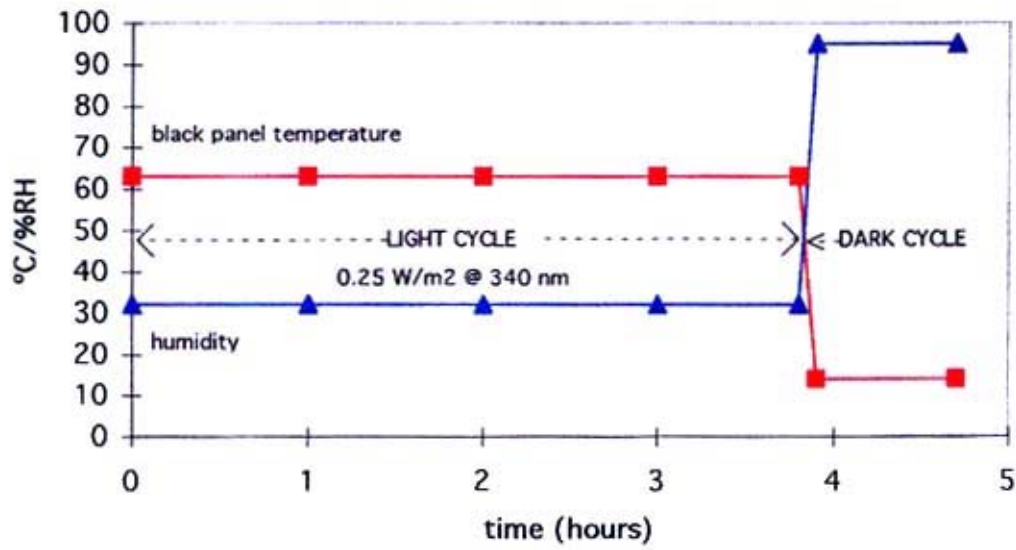
Results of infrared spectroscopic investigation, Py-GC/MS, and XRD further indicate that understanding of complex chemical interactions between individual coatings and substrates is essential in order to piece together this puzzle. Preliminary chemical characterization of coating/metal interfaces showed that significant differences in the chemical character of some coatings exist at the interface as compared to the bulk. Further investigation of this type should reveal valuable, even essential information regarding specific coating/substrate interactions and performance. Further chemical analysis is also necessary in order to answer important questions surrounding the effect of BTA and silanes as pretreatments and as a coating additives.

Results of this study may establish guidelines for future investigations. Results suggest several model coating systems which would be interesting for future study in terms of practicality, including: 1)

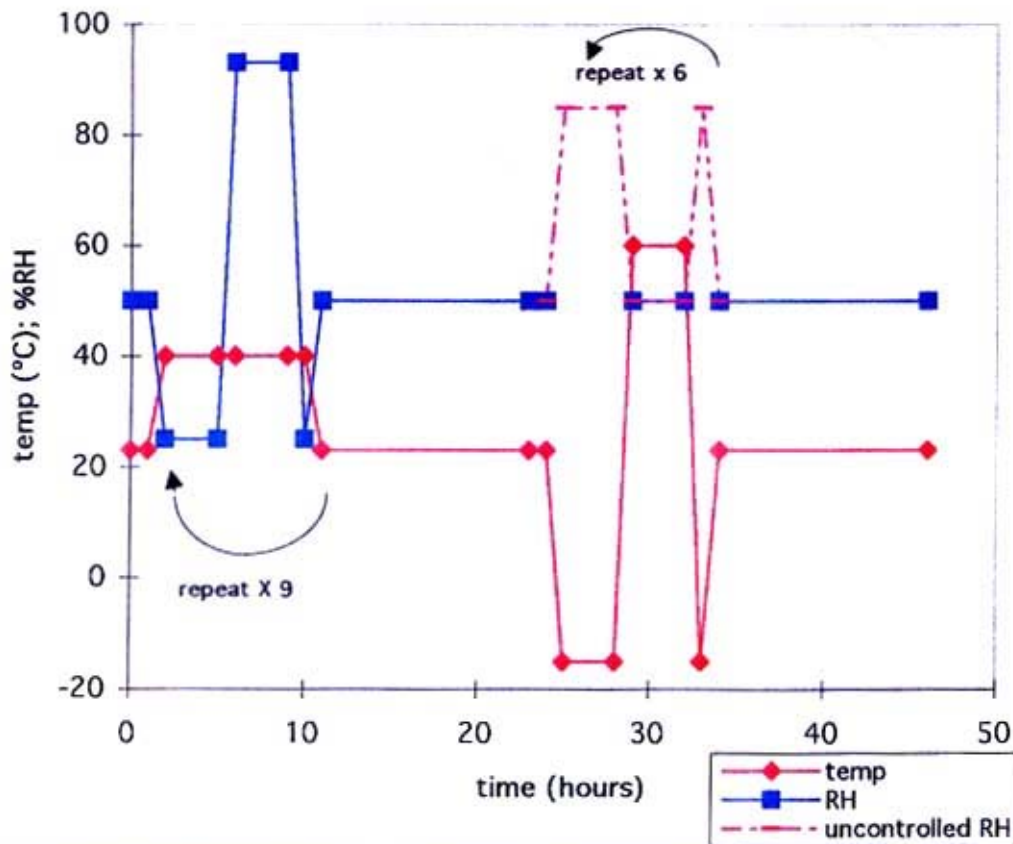
acrylic/acrylic urethane coatings with improved interlamellar adhesion, as well as acrylic urethanes with adhesion promoting treatments, both with a matting agent added as appropriate; 2) Incralac in combination with adhesion promoting pretreatments and/or corrosion inhibitors, plus a top coat and matting agents as appropriate; 3) the NK waterborne acrylic urethane with adhesion promoting pretreatments and top coats; and 4) silicone alkyd with improved aesthetic properties and can be sprayed. Differences in measured physical properties of coatings on polished bronze and patinated copper, and lack of correlation between coating performance on the two substrates, point out the importance of evaluating coatings on different types of substrates. Future investigations should broaden their scope by inclusion of other typical substrates encountered in conservation, including artificially patinated bronze and blast-cleaned, naturally patinated copper. In addition, accelerated weathering and outdoor weathering testing need improved correlation. This type of multiple investigation is essential for elucidation of mechanisms involved in coating performance and should be the focus of future work.



**Figure 1: Xenon-Arc Weatherometer Accelerated Testing Program**



**Figure 2: Tenney Chamber Accelerated Weathering Program with Intermittent "Acid-Rain Solution" Spraying**



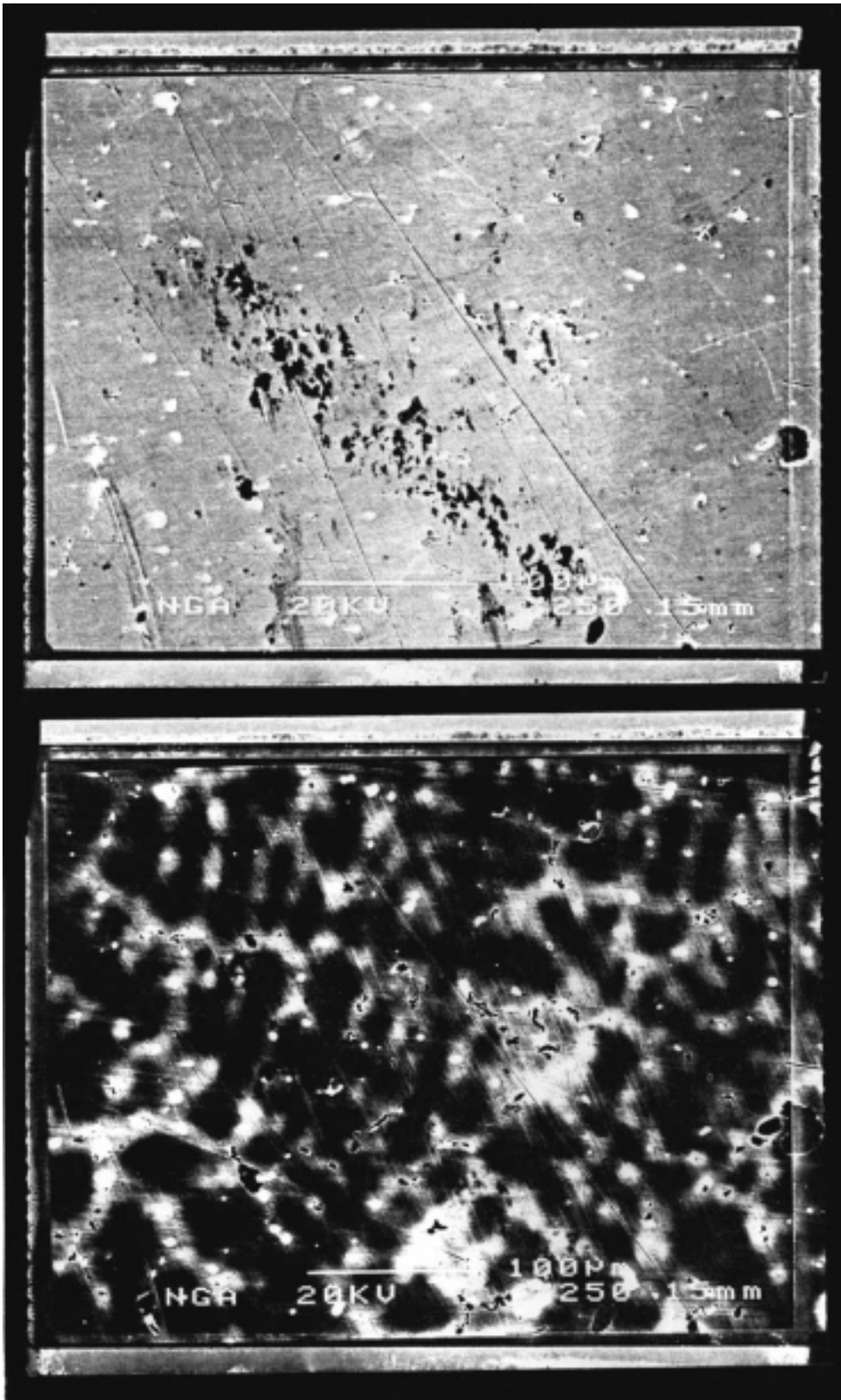
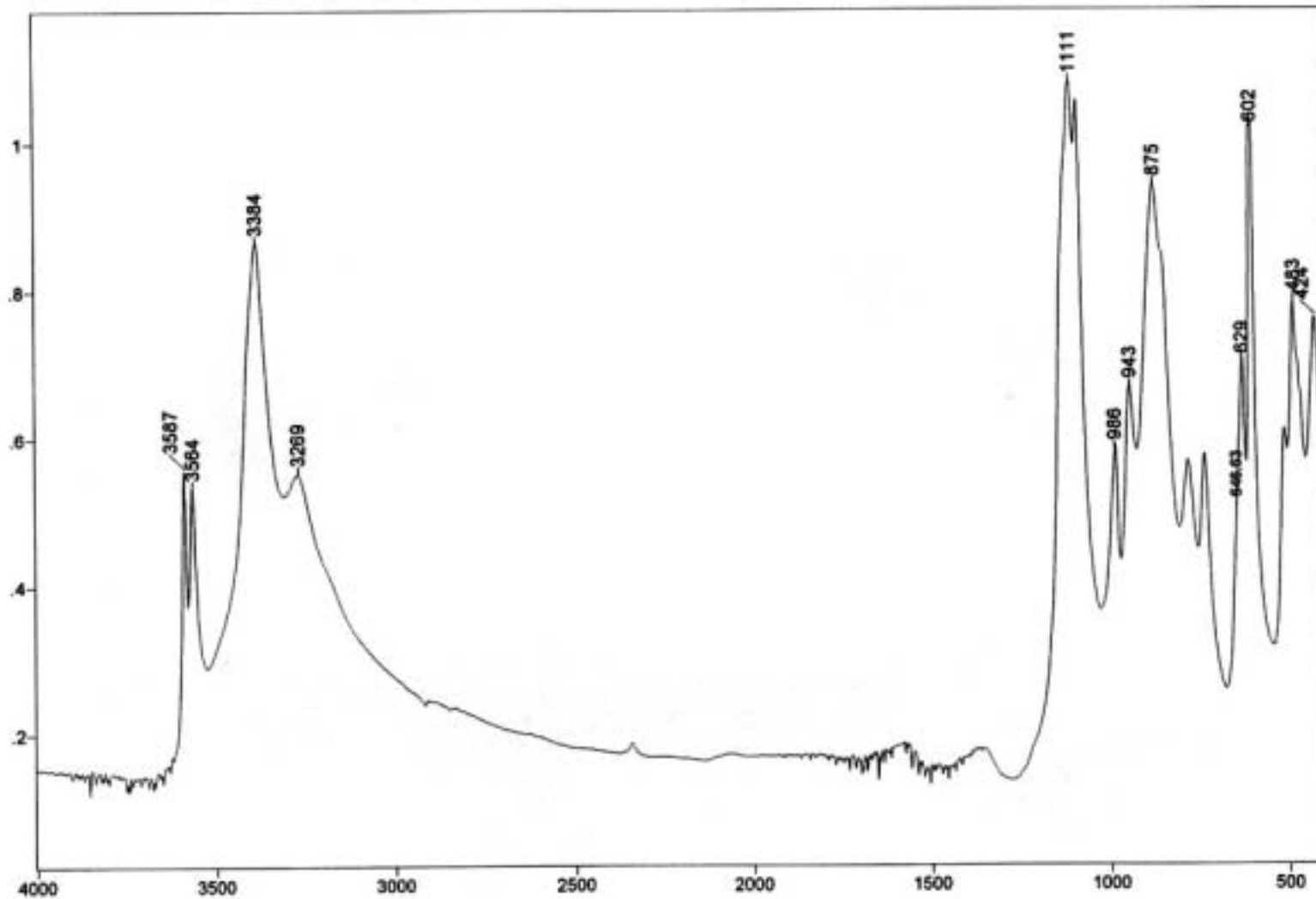


Figure 3: SEM photographs of polished bronze, a) normal image & b) backscattered image (250X)



Absorbance / Wavenumber (cm<sup>-1</sup>)

File # 1 : CURFPAT1 ; sub blank

Figure 4: Infrared spectrum of copper roof patina (KBr, transm.)

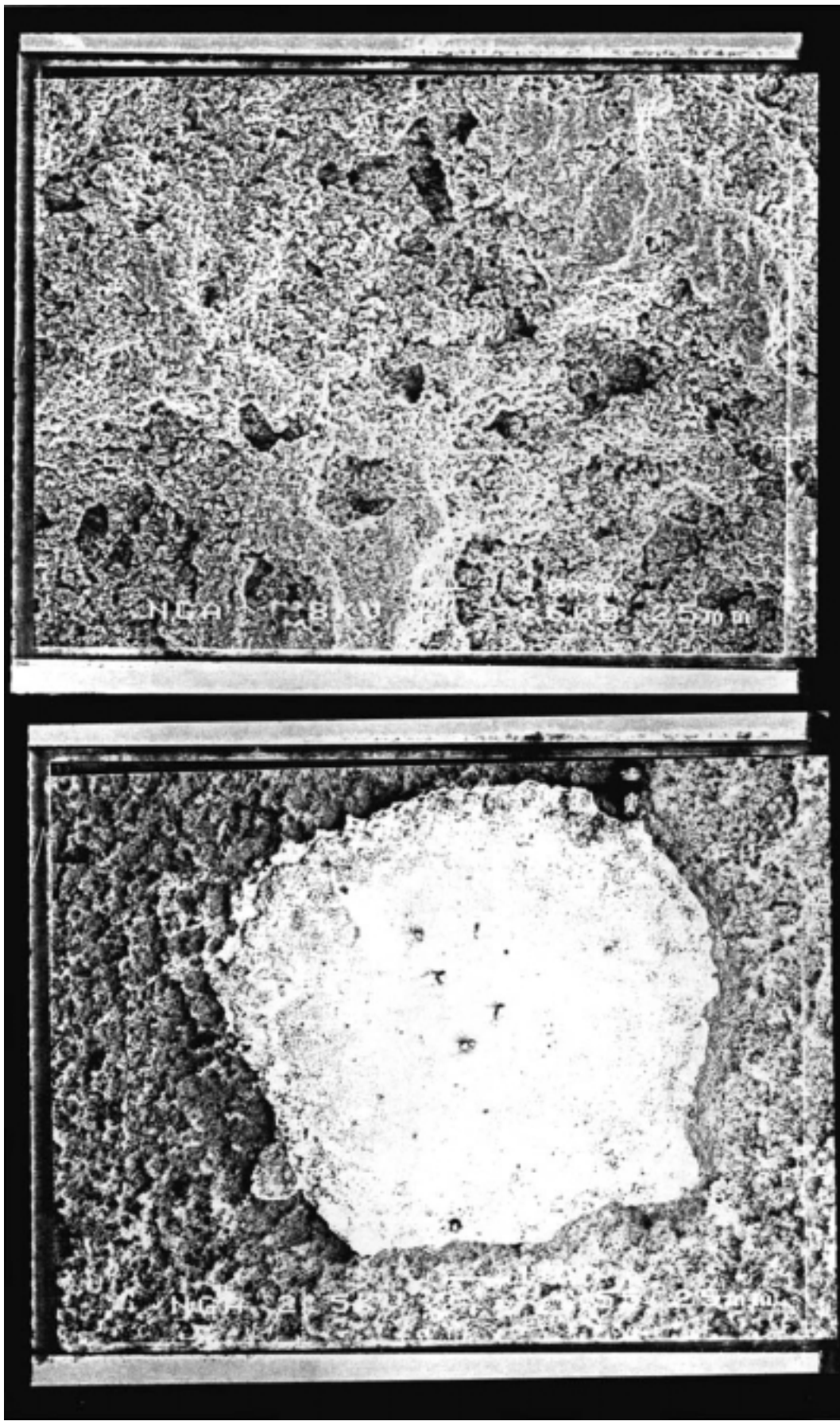
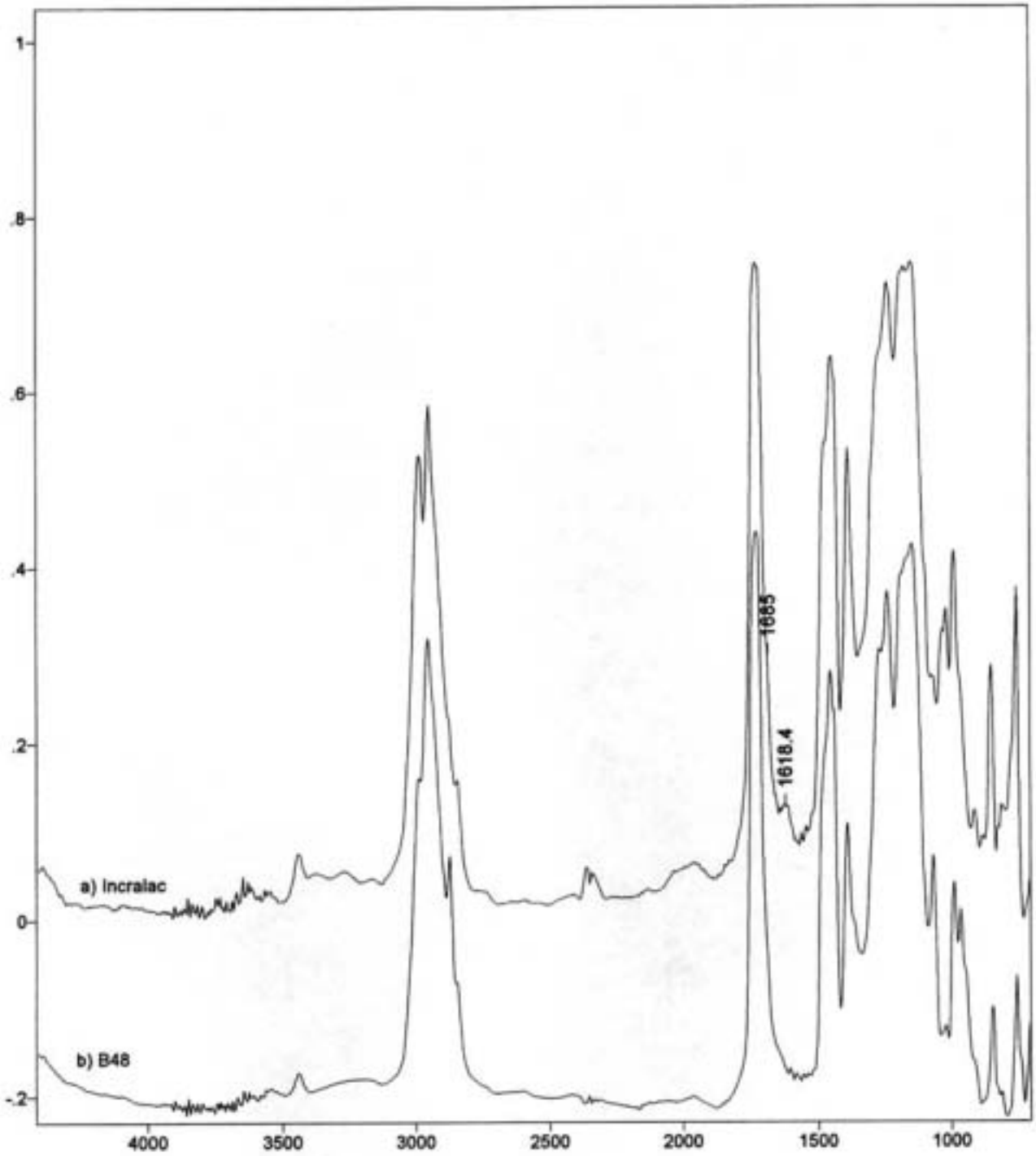


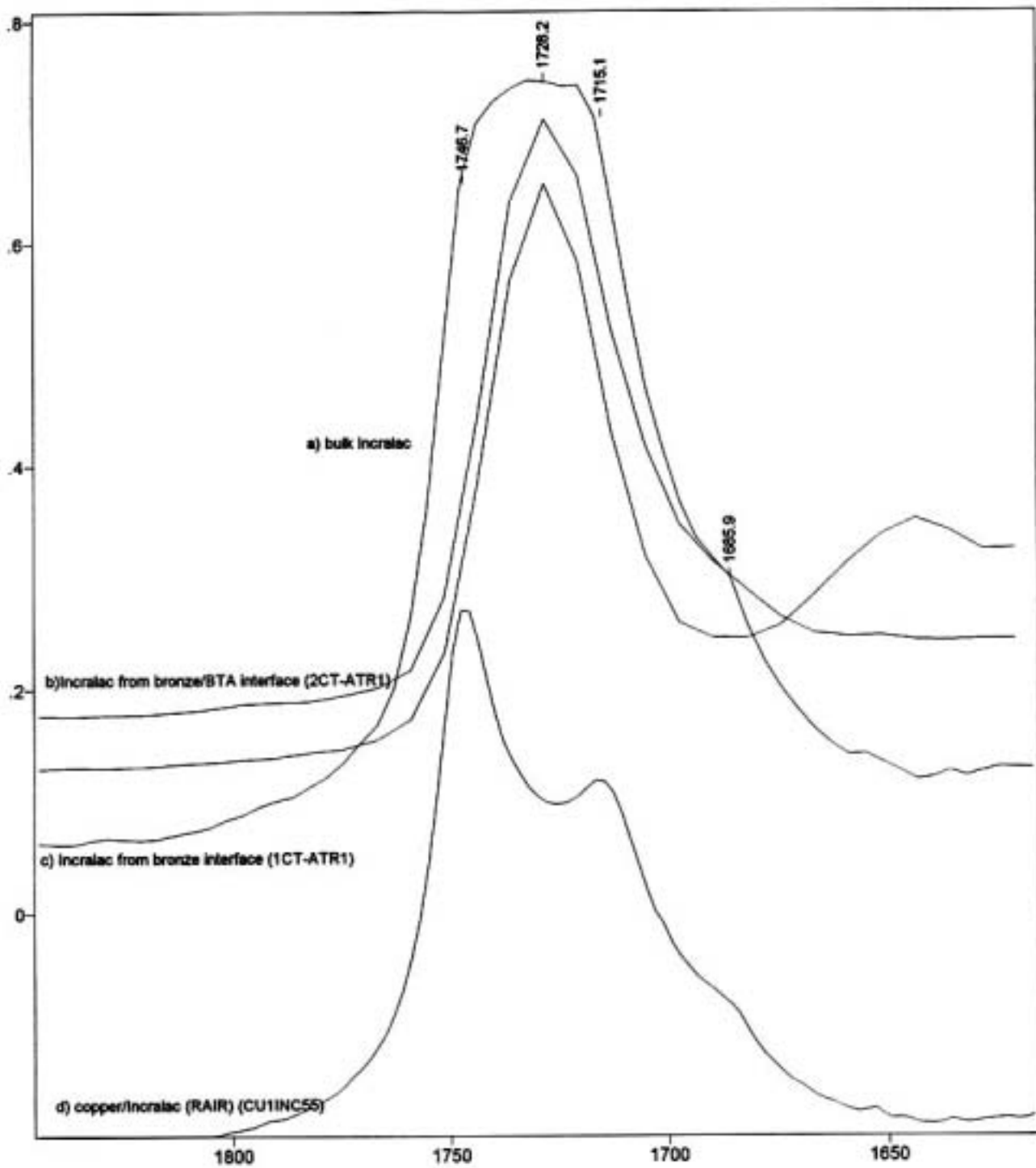
Figure 5: SEM photographs of  
a) copper roof patina and  
b) black spot on green patina



Absorbance / Wavenumber (cm-1)

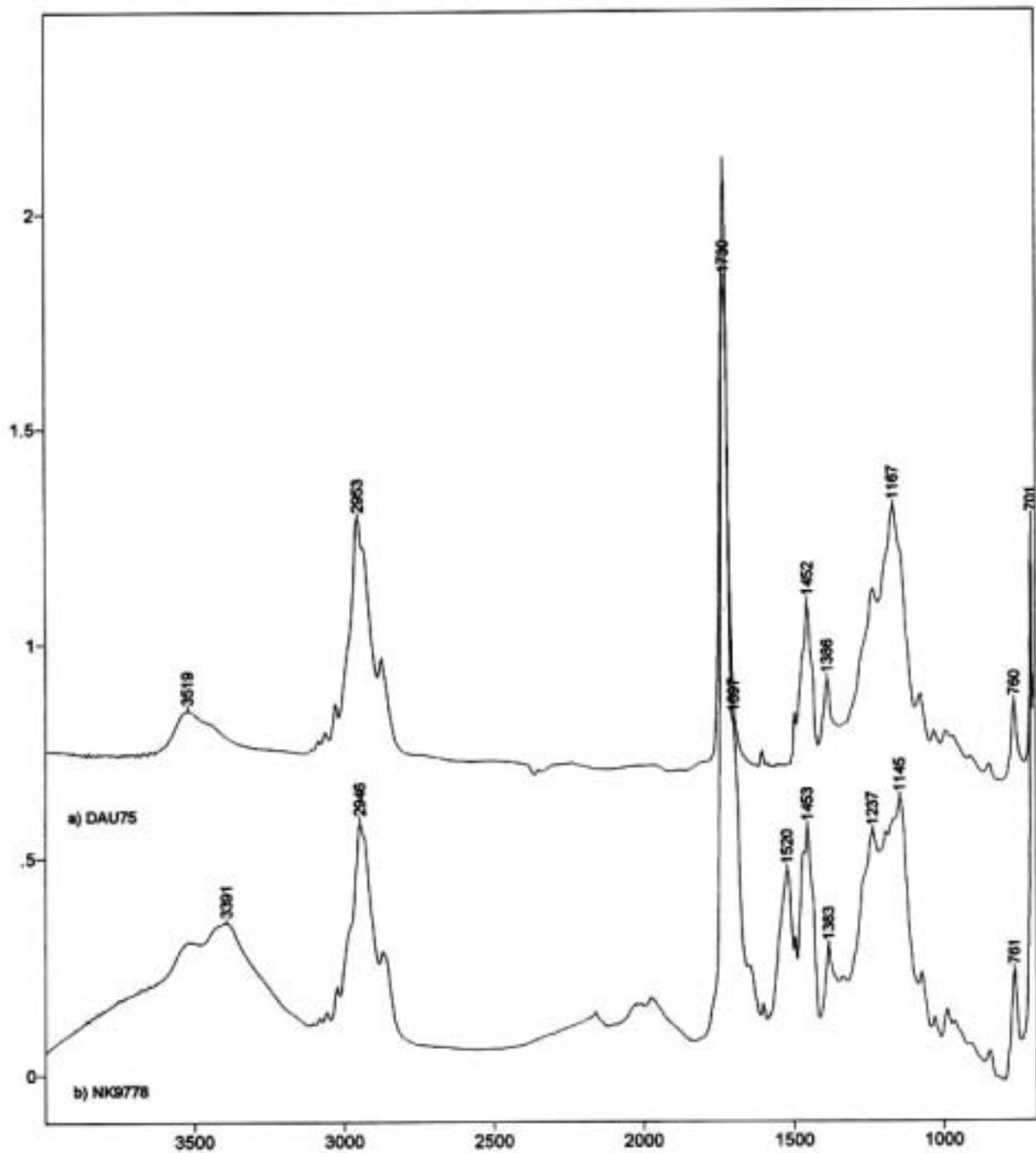
File # 1 : INCRALAC ; B48

Figure 6: Infrared spectra of a) Incralac and b) Acryloid B48



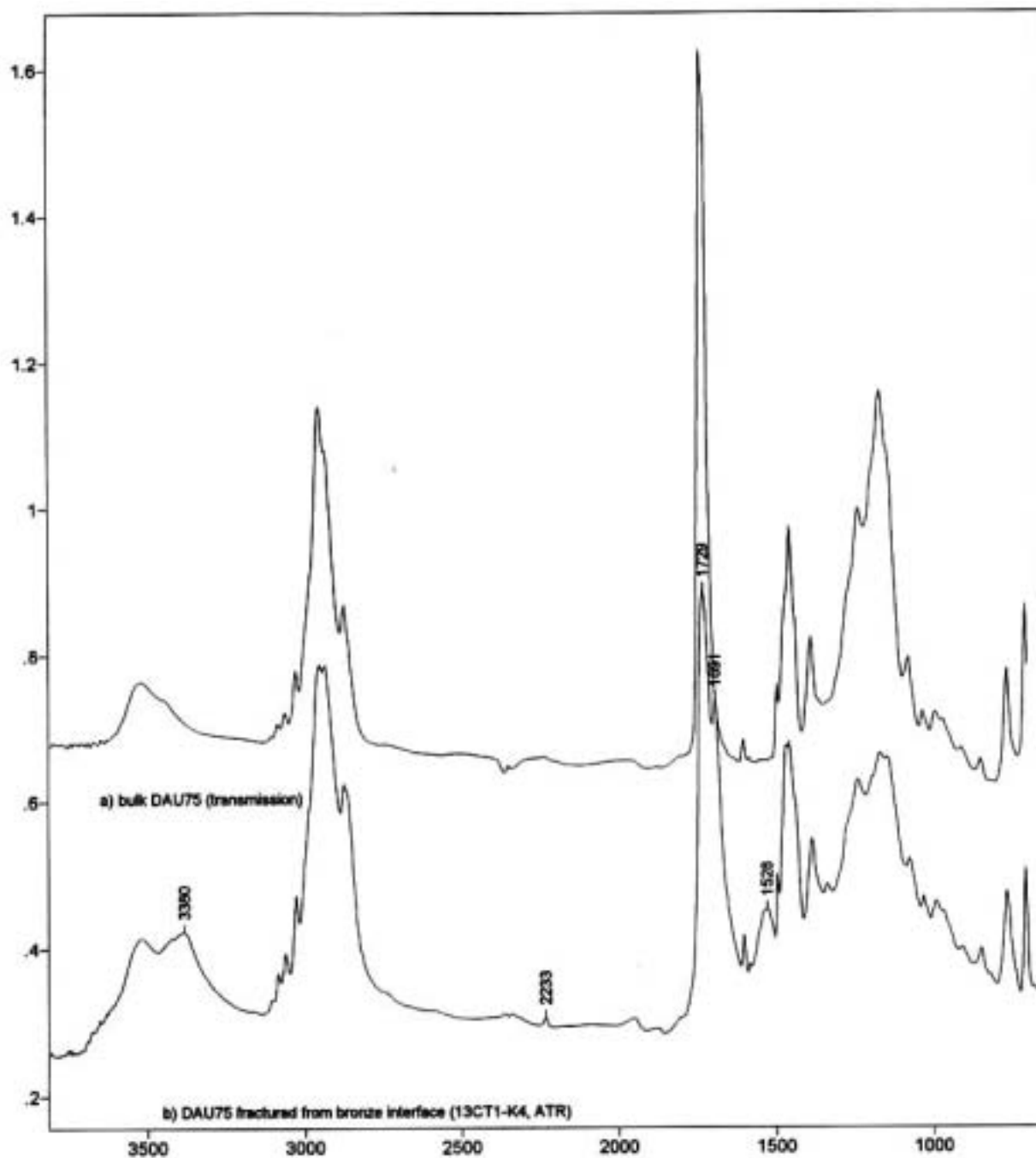
Absorbance / Wavenumber (cm-1)

Figure 7: IR spectra of a)bulk Inralac & b-d) interfaces of Inralac on Cu/bronze



Absorbance / Wavenumber (cm-1)

Figure 8: IR spectra of acrylic urethanes a) DAU75 and b) NK9778

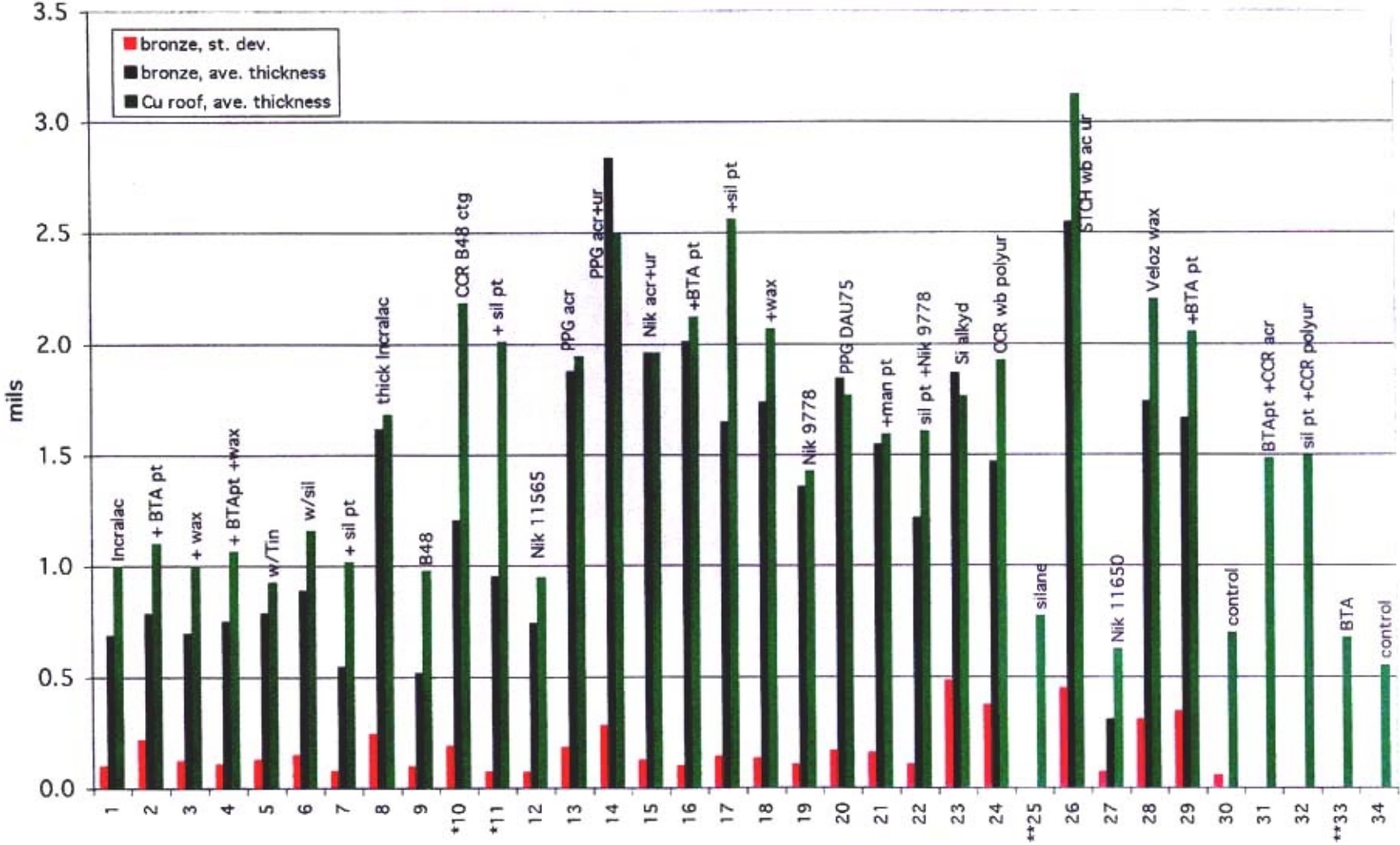


Absorbance / Wavenumber (cm<sup>-1</sup>)

Figure 9: IR spectra of DAU75 a) bulk & b) coating interface fractured from bronze



Figure 10:  
Average Dry Film Thickness of Coatings on Cast  
Bronze and 50-Year-Old Copper Roof Panels

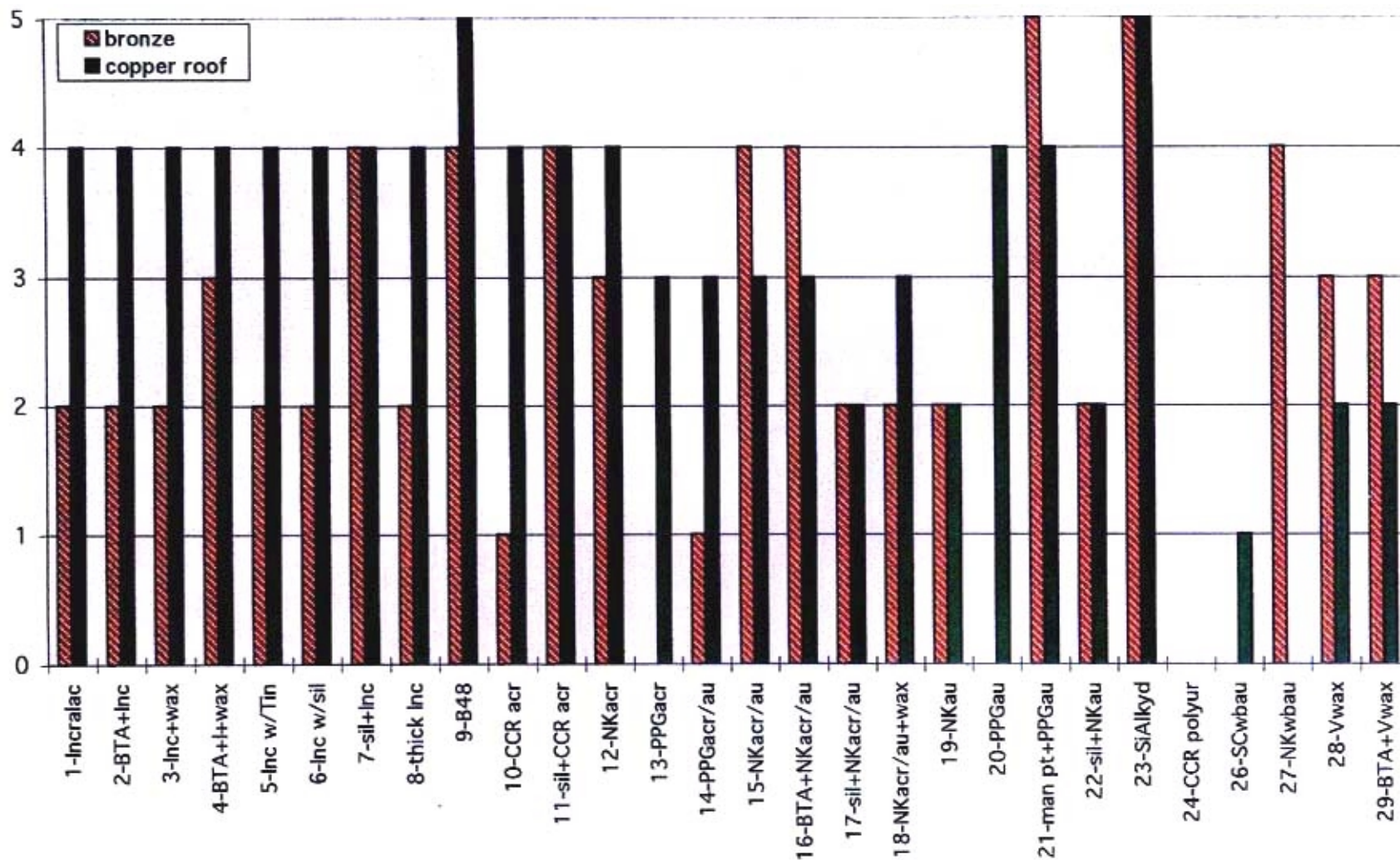


Sample

\*coating applied more thickly to copper roof samples than to bronze  
\*\*silane and BTA film thickness beyond detection limits

Figure 11:

Cross-Cut Adhesion Ratings for Coatings on  
Cast Bronze and 50-Year Old Copper Roof Panels  
Before Weathering\*

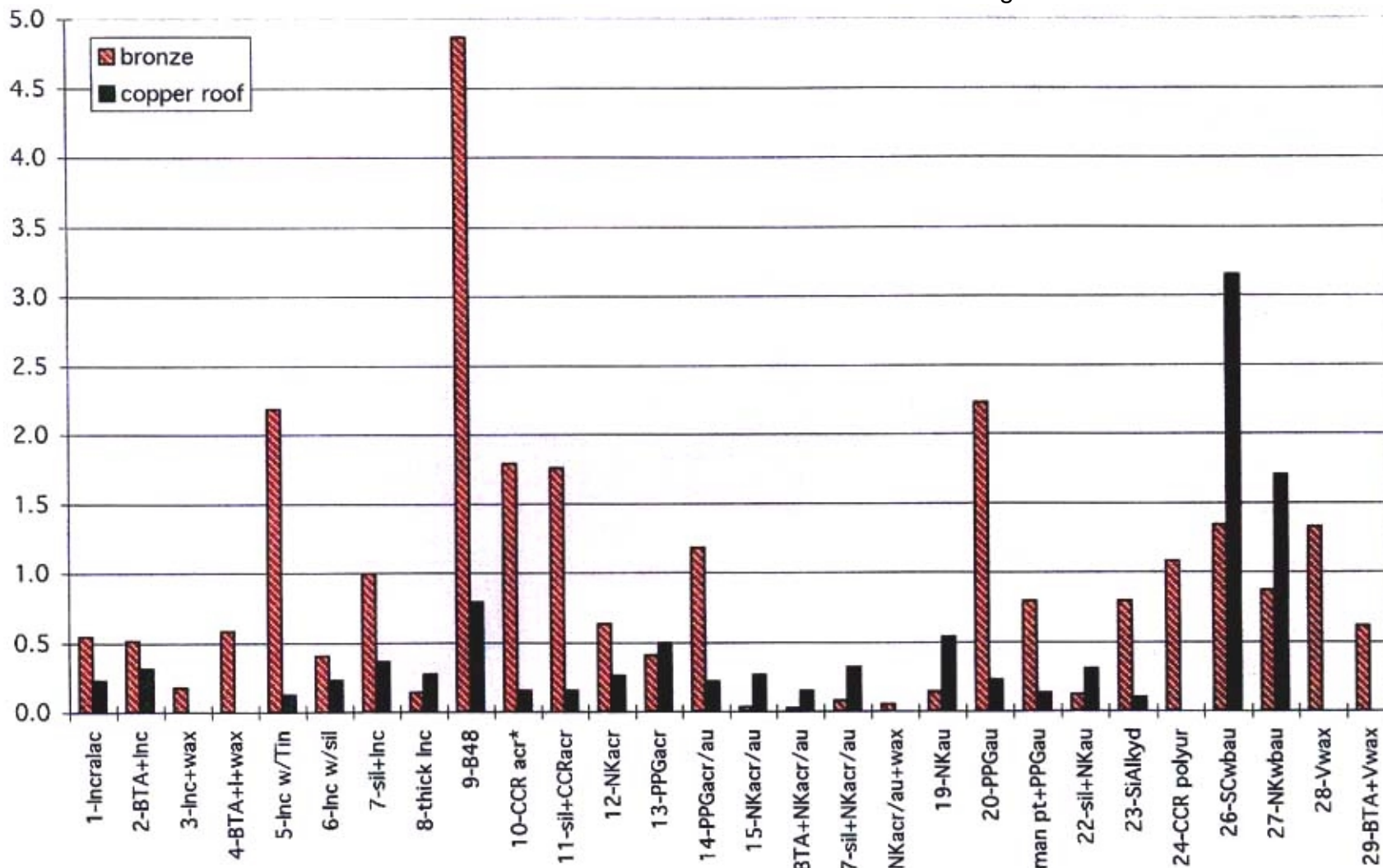


\*#25, silane coating, omitted

**SAMPLE**

Figure 12:

Comparison of Coating Performance on Cast Bronze and 50-Year-Old Copper Roof Panels  
Based on Mean Creepage (mm) and % Area Corrosion  
After 1127 Hr. Accelerated Weathering\*\*



\*CCR acrylic applied in thicker coating on copper roof than on bronze

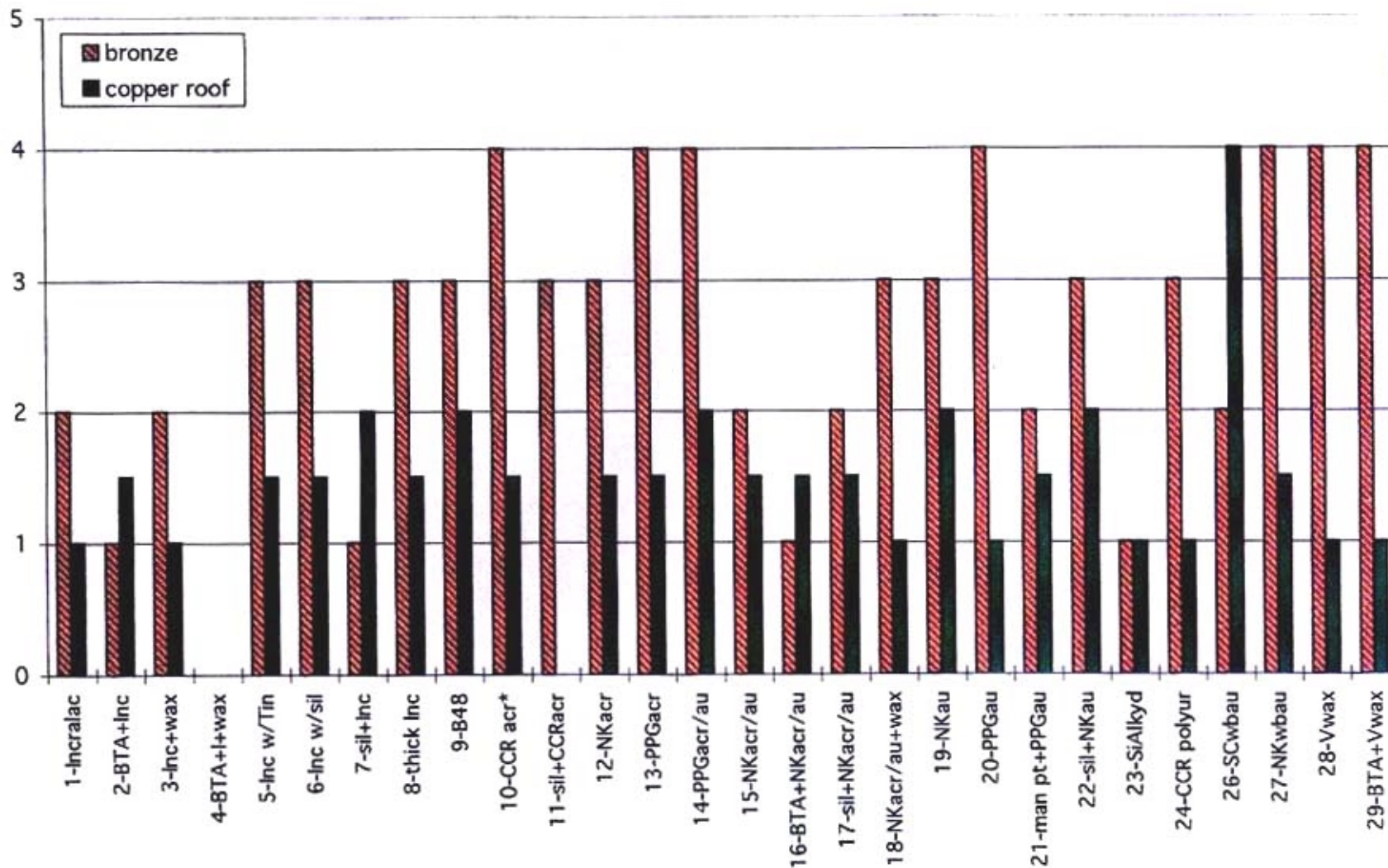
\*\* #25, silane coating, omitted

Sample



Figure 13:

Comparison of Coating Performance on  
Cast Bronze and 50-Year-Old Copper Roof Panels Based on Visual Assessment After  
Approximately 3 Months Outdoor Weathering\*\*



\*CCR acrylic applied in thicker coating on copper roof panel than on bronze

\*\* #25, silane coating, omitted

Sample

Figure 14:

Performance of Coatings on Cast Bronze  
 Based on Corrosion after 1127 Hrs. Accelerated Weathering  
 Shown with De-adhesion Ratings and Average Dry Film Thickness\*\*

