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FROM AN IDEA OF CREATIVITY TO A PRODUCT OF RELIABILITY: UPDATE OF RESEARCH ON ELECTROCHEMICAL TESTING OF EXHIBIT AND STORAGE MATERIALS

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The idea for this project came unexpectedly. Corrosion scientist Rick Corbett of the Corrosion Testing Laboratories, Inc. in Newark, Delaware, helped one of Reedy's students on a research project. To return the favor, Reedy invited Corbett to lunch, during which he mentioned working with industry to test materials used near metal components to identify which materials may cause corrosion. He described a rapid, quantitative test to identify the rate of expected corrosion, performed in less than two hours. Reedy immediately became interested in seeing if his procedures could be applied to conservation problems.

For example, a common conservation problem is that materials used near silver objects often cause tarnish. The typical method for testing materials in conservation is the Oddy test (Oddy 1973; Oddy 1975; Green and Thickett 1995; Lee and Thickett 1996), popular because it is relatively simple to perform; however, it has known drawbacks (Green and Thickett 1993; Reedy et al. 1998). For example, there are many variations on how the test is performed, and these can affect results; the test is not always reproducible; and it takes 30 days to complete, not always realistic for exhibit designers who may need to make faster choices about their materials.

Rick Corbett mentioned that in industry, tests similar to Oddy tests were once in fashion, but long-ago were found to be impractical and likely to be inaccurate (Shepard et al. 1985). Experiments in industry have shown such exposure tests to be unreliable unless more complex standardized procedures can be followed that include use of an adequate number of replicates (at least five) for test materials and for controls, use of ranking tests rather than simple comparisons of specimens to controls, grading by replicate judges rather than by a single individual, blind testing to avoid bias, and application of non-parametric statistical tests on the data (Crume 1985). In many situations it simply is not feasible to conduct 30-day tests.

Instead, industry now relies on a variety of electrochemical testing methods (Siebert 1985; Silverman 1994). Since corrosion is a process involving electrochemical oxidation and reduction reactions between a metal and an electrolyte solution (which may be a very thin film of moisture on a metal surface in the case of atmospheric corrosion), electrochemical methods can be used to study and measure corroding systems. These methods have undergone rigorous testing for a variety of industry applications (Baboian 1976; Mansfield and Bertocci 1981; Baboian 1986; Tait 1994).

Typically the corrosive agents in a test material are extracted in boiling water. The extract solution is then placed in a test cell containing a coupon of the metal of interest (called the working, or test, electrode). Electrochemical reactions characteristic of a specific metal-solution interface occur at the surface of the metal, causing corrosion. These reactions create an electrochemical potential (amount of electrical force, or energy, in the system) called the corrosion potential (E_{corr}), measured in volts. The test cell also includes a reference electrode (such as a calomel electrode), and an inert counter, or auxiliary, electrode (such as graphite or platinum, to pass current to and from the working electrode). The electrodes are connected to a computer containing potentiostatic boards that control the corrosion testing (Fig. 1).

Figure 1. A typical electrochemical testing system, including a test cell containing an electrolyte, working electrode, reference electrode, and auxiliary electrode; and a computer with potentiostatic boards installed.

E_{corr} is compared to the potential of a known reference system (voltage difference between the working electrode and the stable reference electrode). However, at E_{corr} the flow of electrons at the anode (where the metal is oxidized, releasing electrons into the metal) and at the cathode (where a solution species is reduced, removing electrons from the metal) are equal, giving electronic neutrality. In order to measure the corrosion current and estimate a corrosion rate, a voltage applied externally by the potentiostat shifts the current in either the anodic or cathodic direction. When the potentiostat expends electrical energy to shift the metal from its natural corrosion potential, it stimulates either the oxidation or reduction reactions, upsetting the electron balance of E_{corr}; a process called "polarization." An electrode maintained at a potential other than E_{corr} by an external instrument is called "polarized." Under polarization conditions, an oxidation or reduction reaction predominates and a flow of electrons either to or from the metal gives rise to a current. When polarization is performed in a controlled and systematic manner, the resulting corrosion current, or I_{corr}, can be measured (in amps or microamps) and related to the corrosion rate.

The measured corrosion current can be plotted as a function of the applied voltage. Using appropriate formulae, this measured current can be translated into an anticipated rate of corrosion, usually in mils of penetration per year (mpy). Initial experiments showed that this method seemed to work with our metals of interest and exhibition materials, giving high corrosion rates for materials expected to perform poorly and low rates for good materials. Then, after waiting a long time for initial grant funding to come through, a larger array of tests were performed. Several extraction methods (water, methanol, and 50/50 water/methanol) were tested. It was found that water seemed to extract the maximum amount of corrosive agents for most (although not all) materials. Several types of metal were also tested, as all have different ranges of corrosion rates. For example, the corrosion rates for lead ranged from 0.02 mpy for the most compatible materials (such as Medex particle board) up to 8.25 mpy for the most damaging

materials (such as liquid hide glue). In contrast, the rates for silver were much lower, ranging from 0.00 mpy for the most compatible materials (such as Marvelseal) up to 0.145 for the most damaging (such as cardboard). The rates for copper fell in between, with a low of 0.03 mpy for compatible materials (such as Marvelseal) up to 3.62 mpy for damaging ones (such as PVA adhesive) (Reedy et al. 1998).

Although the results were promising, many questions remained unresolved before this method could be routinely applied in a conservation lab. The types of metals, materials to be tested, and amount of acceptable corrosion in industry are different from conservation needs, so industrial methods cannot be transferred directly. For example, in industry, penetration rates of less than 1 mpy are generally considered outstanding, 20-50 mpy are considered fair, and 50-200 mpy are considered poor (Shaw 2003). In contrast, for materials of interest to conservators, unacceptable visible tarnish appears on silver at much lower than 1 mpy, and the worst material (liquid hide glue) on the most reactive metal (lead) produced only 8.25 mpy.

Again the specter of funding loomed large. Bischoff's lab was subsequently able to carry out a series of experiments to continue this work. In the summer of 2000, a modest amount of funding was secured to continue the development of this method with Jason Bustamente and Marc Walton. Although the earlier work had demonstrated that this method showed great promise as a replacement for the Oddy test, there were still many unanswered questions.

The primary question of concern was: "Could any of the procedures be standardized?" The first project tackled was to standardize the extraction procedure. Fig. 2 shows Reedy and Corbett's method, which involved extracting the test material with boiling water in a beaker (American Society for Testing and Materials 1984). Although this is a good, low-technology method, there was concern that some of the volatile materials were being lost when boiling samples in an open beaker. It was felt that continuous aqueous extraction in a partially closed system might avoid this problem, as well as remove more of the "corrosive" materials. Fig. 3 illustrates the Soxhlet continuous extraction setup that might solve this problem. The amount of time needed for optimum extraction was determined, but evaluation of which procedure is actually more effective has not been completed.

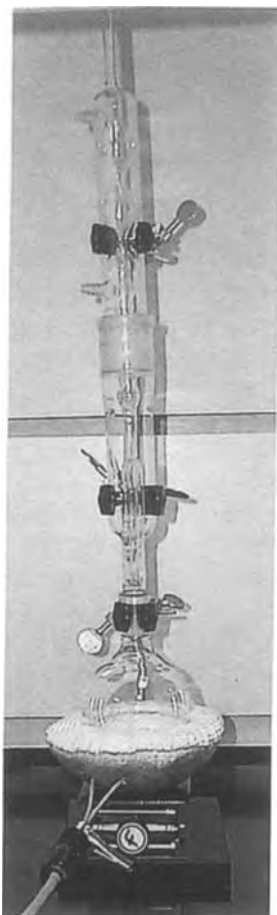Figure 2. Simple boiling extraction procedure.

The second project tackled was standardization of the working electrode design and its care. Because the surface of the working electrode is easily fouled, it needs to be polished between each polarization resistance measurement. Also, because the electrode surface cannot be polished by hand consistently, it was thought that automatic polishing between runs would provide a consistently clean surface.

The first electrode designed, labeled "old design" in Fig. 4, was a single assembly. This one-piece design made it difficult to reproducibly polish the electrode surface between runs. The second design is the one labeled "new design" in Fig. 4, a schematic of which is shown in Fig. 5. This new design allowed easy removal of the assembly containing the electrode surface for automatically polishing with a Buehler Minimet Polisher. The great advantage of the new design is that a standard cleaning and polishing regime can easily be performed on the removable assembly.

Although the new design had some advantages over the old, the performance of the two electrodes needed to be compared. Polarization resistance measurements (20 in all) were made on aqueous potassium chloride solutions and statistical analysis was performed on the results. Fig. 6 shows the average corrosion current (I_{corr}) and corrosion potential (E_{corr}) for 20 measurements on each electrode, along with standard deviations for these measurements.

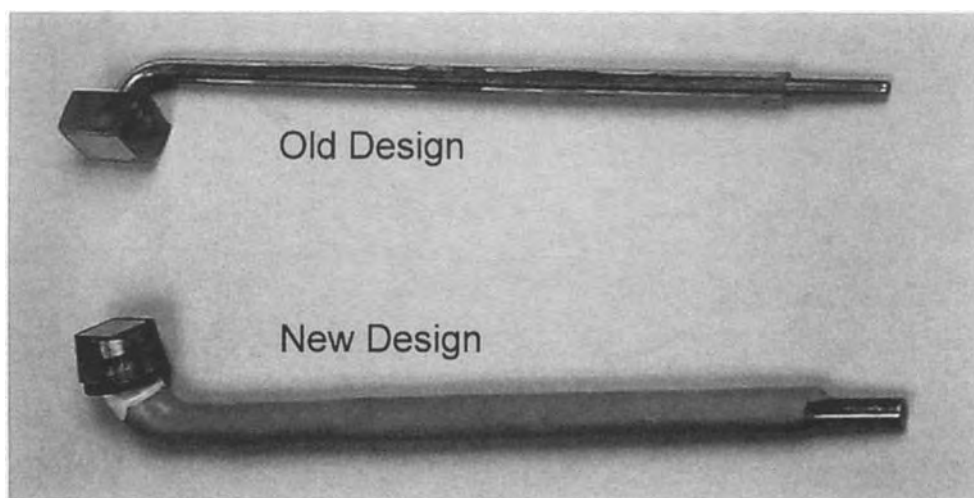Figure 3. Soxhlet continuous extraction procedure.

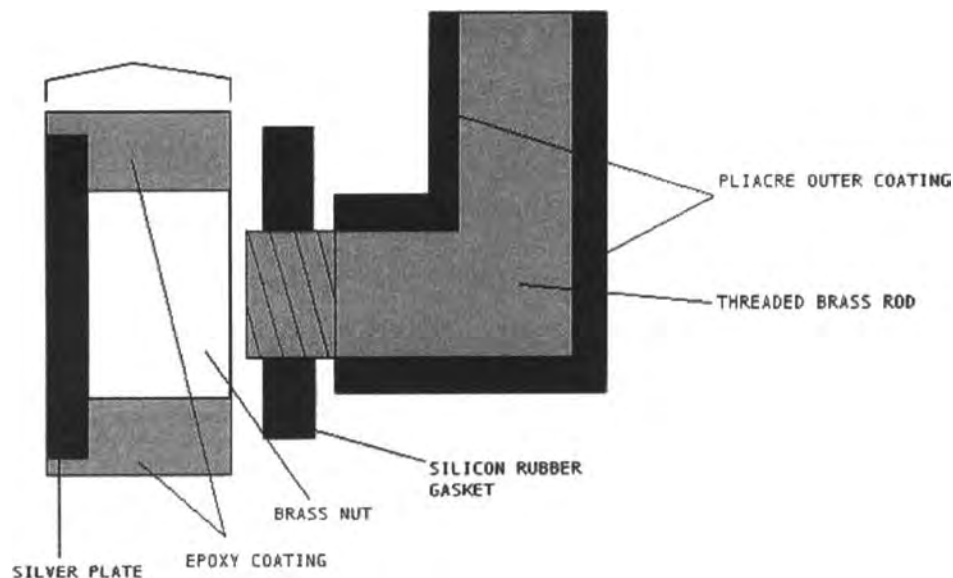Figure 4. Comparison of two electrode designs.

Figure 5. Details of new design for working electrode.

As Fig. 6 illustrates, the results for the two electrodes are comparable. These results confirm that our second design was an improvement over the first because it is easier to consistently clean the electrode surface between runs.

	Old Design	**New Design**
Average I_{corr} (a/cm^2)	2.102×10^{-6}	2.451×10^{-6}
Standard Deviation	4.397×10^{-7}	7.116×10^{-7}
Average E_{corr} (mV)	0.071	0.082
Standard Deviation	0.015	0.024

Figure 6. Comparison of electrode performance.

Reproducibility

The second question of concern was: "Is this method reproducible?" The answer to this question is critical since, if the method is not reproducible, then it is of no more value than the Oddy test. The approach taken by Bischoff, Bustamente and Walton for examination of the data differed

from that used by Reedy and Corbett. Bischoff et al. plotted various results obtained from polarization resistance measurements to see if any of the data would cluster into groups of known acceptable and unacceptable materials. The best correlation was between the corrosion potential (E_{corr}) and the corrosion current (I_{corr}). Corrosion potential is the potential at which the electrochemical reactions at the positive and negative electrodes are equal, and the corrosion current is a measure of the propensity of a solution, for example, the aqueous extract of the storage or exhibit material, to cause corrosion of a metal object. When the corrosion current is plotted against the corrosion potential for extracts of oak and acrylic, as shown in Fig. 7, the data points for the oak (unacceptable material) clustered in one group and those of the acrylic (acceptable material) clustered in another.
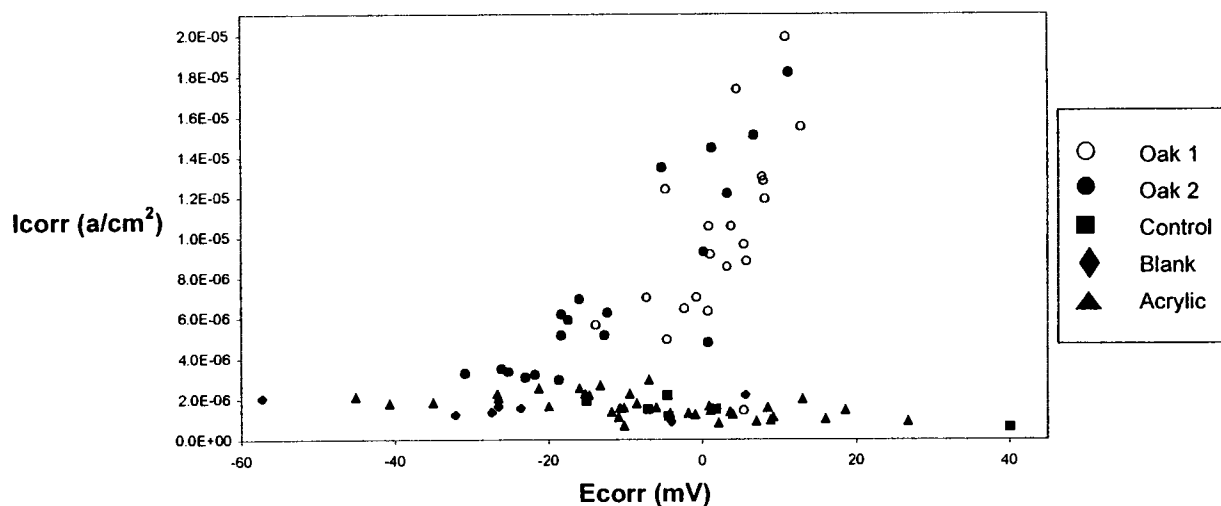

Figure 7. I_{corr} versus E_{corr} for oak and acrylic.

Because the data appeared to show a high degree of scatter, it was thought that reproducibility might be improved by the addition of an electrolyte such as potassium chloride. Instead, the plot of I_{corr} versus E_{corr} (Fig. 8) showed increased scatter of the data for the acrylic extract with added potassium chloride. It is possible that potassium chloride was a poor choice and so samples of acrylic with other electrolytes such as sodium nitrate must be run.

Because electrochemical reactions are temperature dependent, polarization resistance measurements were run on extracts of oak under isothermal conditions (Fig. 9). Statistical analysis showed essentially no difference between measurements made under ambient (variable) or isothermal conditions.
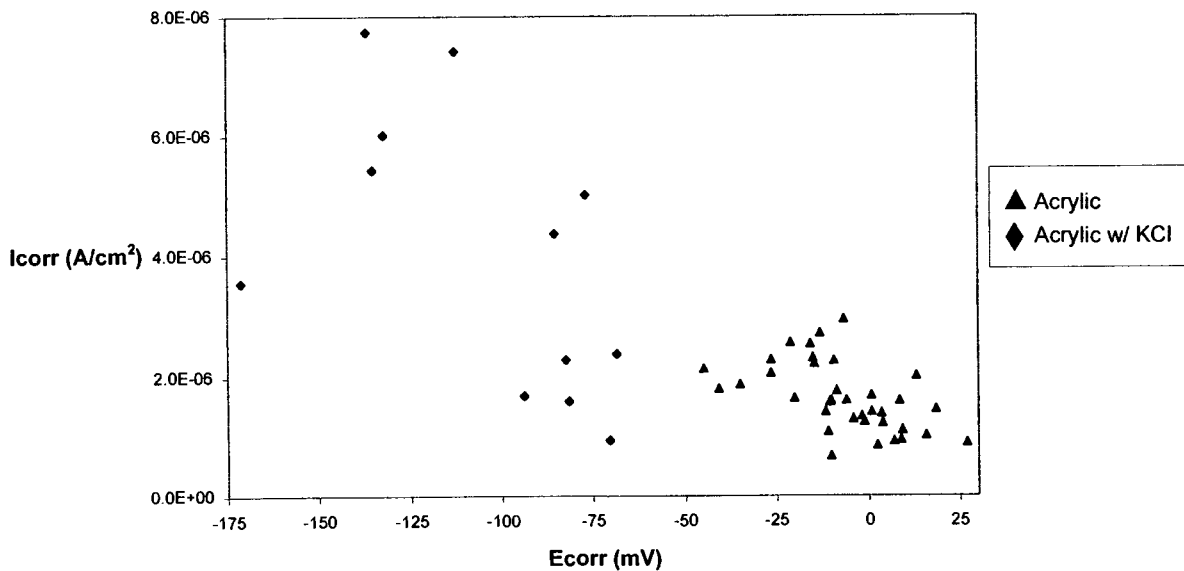
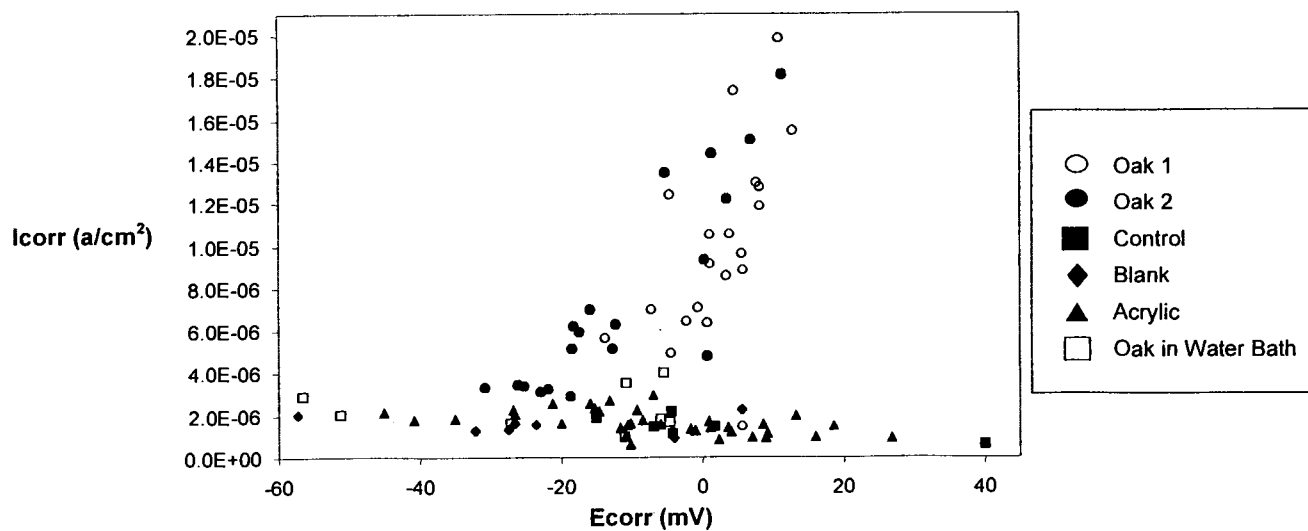Figure 8. I_{corr} versus E_{corr} for acrylic with aqueous KCL

Figure 9. I_{corr} versus E_{corr} under isothermal conditions.

Unfortunately, once again funding ran out for this project. At this point the electrode design has been improved, making it easier to clean between runs without sacrificing electrode performance. It has also been demonstrated that there has been no improvement in the reproducibility of the

measurements either with addition of an electrolyte or by taking the measurements under isothermal conditions. The evidence is still convincing that this method will prove to be a significant advantage over the Oddy test, but there is still much work to be done.

The next phase of research will include the following steps:

> Continue to develop the experimental methodology, including consultations with electrochemists as needed. In order to test the reproducibility of polarization resistance tests, replicates will be analyzed and repeated measurements performed independent of extraction method.

> Continue also to develop the extraction procedures and compare the effectiveness of the two methods described earlier.

> Investigate the need to use different extraction protocols (for example, using methanol or a water/methanol procedure) for certain classes of materials.

> It is unclear to what extent materials extracted in water are the same materials that evolve during off-gassing. Plans include identification of both off-gassing and extracted materials to lay this question to rest.

> Now that a good design for a working electrode has been developed, a standard cleaning and polishing protocol will be developed.

> Because electrical noise may affect reproducibility of results, the use of a Faraday cage for shielding the test cell will be investigated.

> Five different cell designs will be tested to compare their ease of use, and also to see if some designs have any effect on reproducibility of results. Some test cells are rather expensive, others are quite affordable; and some cells require a more elaborate working electrode design while others use only a simple flat piece of metal. If various electrochemical cells are found to be comparable in reproducibility, then those that are relatively easy to use and inexpensive would be preferable for most conservation uses.

> The extent to which crevice corrosion may be developing along the edges of the working electrode, a known hazard that can seriously affect accuracy and reproducibility of measurements, must be tested, as well as various masking regimes to prevent crevice corrosion.

>> Plans are to incorporate calibration of the reference electrode to a laboratory reference standard in between each test, to ensure that no changes are occurring that could affect reproducibility.

>> Different corrosion measurement techniques (linear polarization, poteniodynamic polarization with corrosion rate determined by Tafel extrapolation and/or Tafel analysis) need to be compared to determine which is most satisfactory for conservation applications.

>> Many samples of materials whose acceptability for use in storage or exhibit cases is already known still need to be tested, so that the ranges of results for acceptable and unacceptable materials can be defined. Only then can a database of known exhibit and

storage materials be created and new materials tested.

Once a reliable method has been developed, a draft "users" manual needs to be created. Plans are to identify pilot test sites and then train staff at these sites. Feedback from the pilot test sites will then allow the method to be improved.

None of this will happen without financial assistance. Multi-year funding must be obtained to upgrade outdated equipment and software, hire research assistants to help with the many experiments that must be conducted, and pay for consultant fees and/or contract analysis. Funding will also be needed for travel and training for staff at pilot test sites. Finally, the work of writing, editing, and publishing the manual will need to be funded.

The final goal, of course, is to bring this method into general use by the conservation community. This will require long-term coordination, otherwise the method will remain as a dusty piece of equipment in the corner of the laboratory. So, the path from an idea of creativity to a method of reliability is a long one. This work has put Reedy and Bischoff's labs on the path, but only funding and the combined efforts of Reedy and Bischoff will help to guide the way to a method accepted and used by our professional community.

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Electrochemical test cell (micro-cell) and accessories, Princeton Applied Research, CN 5206, Princeton, NJ 08543, 609-895-0100.

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