Smart Appliqués for Corrosion Protection and Health Monitoring

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ABSTRACT

The tropical marine environment is highly corrosive and improved corrosion protection and control (CPC) methods are needed to protect valuable and critical assets and infrastructure. A solution to this corrosion problem is smart appliqués that provide excellent corrosion protection and health monitoring to alert an inspector if the appliqué has been damaged or has deteriorated. These smart appliqués are peel-and-stick fluoropolymer films with a sensor electrode and pressure sensitive adhesive. Aluminum and steel panels with smart appliqués were exposed to 2000 hours of salt fog. No corrosion was observed on any of the defect-free specimens. On the scribed aluminum panels, no undercutting of the appliqué was seen at the scribe. On the scribed steel panels, undercutting did not exceed 1-2 mm. Electrochemical impedance spectroscopy (EIS) measurements using the embedded sensors allowed health monitoring. The sensors easily detected the early stages of corrosion resulting from a scribe in the appliqué and from a backside defect. For the backside defects, the sensor measurements correlated with the amount of corrosion present. These sensors would easily detect any damage to the appliqué or poor appliqué installation before any damage to the structure occurred.

Keywords: appliqué, corrosion, sensor, electrochemical impedance, paint replacement film

INTRODUCTION

Corrosion of test assets and other structures used by the Missile Defense Agency (MDA) and other DOD branches is an ongoing maintenance and reliability issue. Corrosion is estimated to cost DOD over $20B per year – the greatest factor in lifecycle costs.[1] The cost of repairs, maintenance, and replacement is a direct cost. The loss of lives and readiness are additional indirect costs, which cannot be assessed in dollar amounts, especially in time of a national emergency or wartime. Corrosion is aggravated by the need to operate in some of the most corrosive environments. MDA, for example, must station test assets at remote locations at the Kwajalein Atoll in the Marshall Islands. This includes critical test assets such as radars, as well as civil and base infrastructure (e.g. buildings, water and fuel systems, power plants, etc.). Marine or coastal locations, especially those in hot or equatorial climates, are particularly corrosive as indicated in Figure 1.[2-4] Remoteness of facilities further excoriates the situation by limiting the staff available to perform frequent maintenance of structures and systems.

The corrosiveness of the tropical Pacific environment is illustrated in Figure 2. Corrosion made a half-million-dollar boom truck unsafe and useless at Kwajalein Atoll after only 3 years. The constant salt

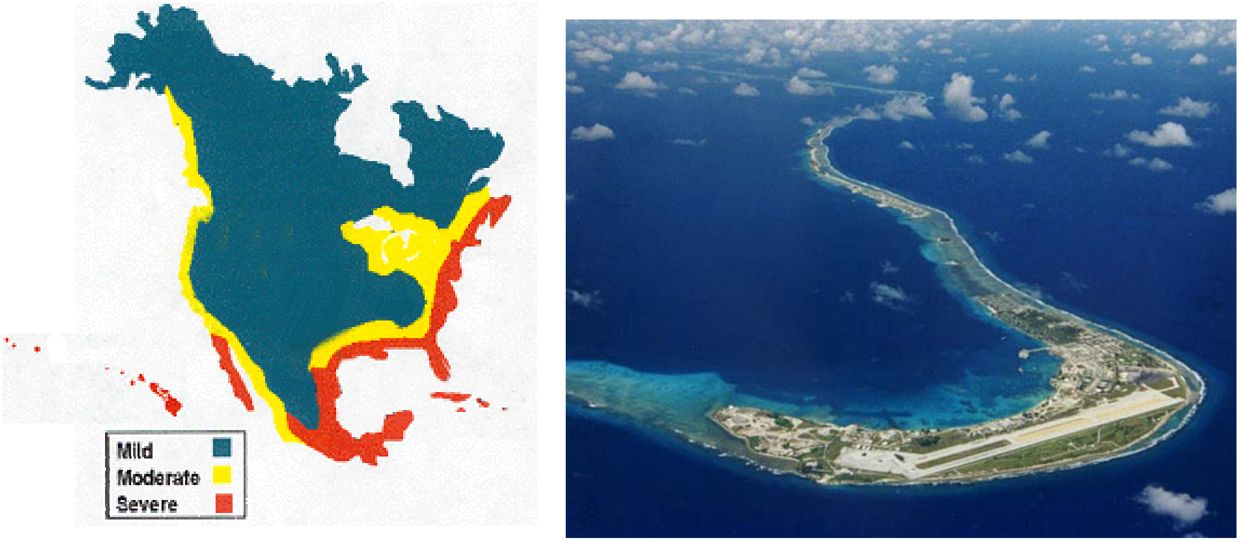

Figure 1. Left) Aggressiveness or corrosivity of the environment for Canada, Mexico, and the United States. Right) Aerial view of the Kwajalein Atoll in the Marshall Islands illustrating factors contributing to a high corrosivity environment: tropical location, proximity of all locations on the island to the ocean, and low elevation providing no blocking of wind.

spray from the Pacific Ocean corrodes all structures and equipment and dramatically reduces operational lifetime and increases life-cycle costs.

The most common approach to prevent corrosion of metallic structures is paint. Paints can be very effective, but must be considered temporary. They weather, crack, or otherwise degrade or get chipped or scratched. Consequently, painted structures must periodically be repainted – a costly and labor-intensive process that involves environmental issues of waste from old paint (lead, chromates) and volatile organic compounds (VOCs). Furthermore, the presence of a virtual continuous salt spray creates a situation wherein the surface is recontaminated. This is evidenced by repaired and painted areas requiring repeated treatment over short periods. Numerous approaches have been attempted but a long-term solution has been elusive.

Because traditional painting used as a protective and decorative approach to mitigating corrosion suffers

Figure 2. Left: Boom truck on Kwajalein Atoll. Right: Close up of corrosion that made boom truck unsafe and inoperative after only 3 years.

from these drawbacks, there have been significant efforts to modify or develop paint systems to comply with ever increasing air quality and human protection demands. However, parallel efforts have demonstrated that paintless application of films using pressure sensitive "peel and stick" adhesive technology is another corrosion mitigation approach that is gaining momentum.

Although appliqués have proven very successful in corrosion protection, corrosion can sometimes occur from the backside of the coated surface or can also result from improper installation or from intrusion through compromised sections of the film that are not clearly visible to the eye. Consequently, there is a need to have a smart, sensored appliqué whose health can be monitored with appropriate instrumentation. Such procedures would enable condition-based maintenance (CBM), increase system reliability, and decrease cost.

Many corrosion sensors have been proposed and developed.[5-13] Each has its advantages and disadvantages but not all are suitable for incorporation into a smart appliqué. A major disadvantage of many of these is that they are more properly considered corrosivity sensors; that is, they detect degradation of a sensor element and not degradation of the structure of interest. As such, they measure only corrosivity of the environment, but provide no direct information on the condition of the structure of interest. Furthermore, they are consumed as they measure corrosion and therefore have a limited lifetime. Others are too large (thick) to incorporate into a thin appliqué or are not compatible with appliqué fabrication. The electrochemical impedance sensor approach used here has none of these critical disadvantages. The technology is suitable for detection of damage under appliqués in the field and in the laboratory.

DACCO SCI, INC., (DSI) and Integument Technologies, Inc, (ITI) have evaluated and showed the feasibility of a smart appliqué that not only is very effective in providing corrosion protection, but also is capable of health monitoring for condition-based maintenance. This appliqué will track corrosion damage from its early stages, indicate an assessment of current condition, and provide a prediction of future condition based on accelerated laboratory testing. The major innovation of this program centered on the development of a real-time corrosion sensor that is built directly into a peel and stick coating system. Specifically, this program demonstrated a multifunctional appliqué coating system that:

- Is very protective against corrosion
- Involves no VOC emissions during application
- Has multifunctional capabilities
- Directly inspects and assesses the condition of the structure of interest. It does not involve corrosivity sensors that simply detect degradation of a sensor element.
- Detects the intrusion of the aggressive environment well before any irreversible corrosion damage occurs while it is also sensitive to the growth of corrosion products during the more severe stages of damage.

The appliqué is based on fluoropolymer adhesive film technology. The sensor is based on electrochemical impedance spectroscopy (EIS), a well-established laboratory technique known to predict materials performance, but hitherto limited to immersion studies. The electrochemical sensor extends the use of EIS to field applications and allows identical measurements to be taken under service conditions and laboratory testing.

Several fluoropolymer based, paintless corrosion protection systems have been developed over the last several years for applications in the chemical and food processing and transportation industries. These paintless coatings systems, or appliqués, have demonstrated high performance levels for protection from severe chemical, temperature and other corrosive environments.[14-16] Based on initial successes and testing, additional development of these appliqués has focused on the novel multifunctional fluoropolymer appliqués for applications such as:

- Paintless corrosion protection appliqués for aircraft
- Foul release and corrosion protection appliqués for ships.
- Lightning strike protection appliqués for composite aircraft.

Results and developments from these projects include:

- The development of new adhesives containing organic based, environmentally friendly amine corrosion inhibitors.
- The development of an appliqué system that has outstanding adhesion but can be easily applied, removed, and repaired.
- Demonstration of thermal stability of above appliqué system throughout –65°F to 350°F range with adequate adhesion and removal properties.
- Demonstration of outstanding resistance of above appliqué system to various fluids commonly encountered on aircraft, (e.g., hydraulic fluid, JP-8 jet fuel, cleaning solvents, and de-icing agents) even under total immersion for 14-day tests with acceptable decreases in peel adhesion and no delamination.
- Demonstration of outstanding resistance of above appliqué system to QUVA weathering.
- Demonstration of outstanding resistance of above appliqué system to environmental corrosion. Appliqué coated panels were scribed and then subjected to 2000 hrs of Salt Fog Spray (ASTM B-117) followed by 500 hrs of SO_2 Salt Fog (ASTM G-85). Only limited corrosion at the scribed sites was observed with undercutting of appliqué less than 1mm. No corrosion was observed at any other coated sites on 2”x 4” 2024-T aluminum test panels.
- Development of a peel and stick fluoropolymer appliqué system that contains conductive copper or aluminum foil within the appliqué composite. These appliqués were developed for protecting composite aircraft from lightning strikes. Lightning protection capabilities have been demonstrated and show outstanding results. Note, to date, no corrosion of the embedded conducting metals has been observed due to the protection provided by the fluoropolymer outer layer.

In parallel efforts, an *in-situ* corrosion sensor has been developed that can detect the early stages of coating degradation, moisture uptake, and substrate corrosion of painted structures. It is also capable of detecting moisture ingress into a composite and an adhesive joint and detecting decreased bonded area. The sensor, when coupled with a portable potentiostat, is suitable for both laboratory and field inspection. Figure 3 shows a prototype handheld sensor being used to inspect the paint coating on a KC135 aircraft at Hickam AFB. Inspection of exterior surfaces and accessible interior surfaces is readily achievable using the portable sensor shown in the figure. For less accessible components, permanent, painted sensors are available. A single wire and a ground connection allow data acquisition at a convenient point. A variation of this painted sensor is used for the smart appliqués, as illustrated in Figure 4. Here a metal mesh or expanded metal foil is added to the appliqué between two layers of pressure

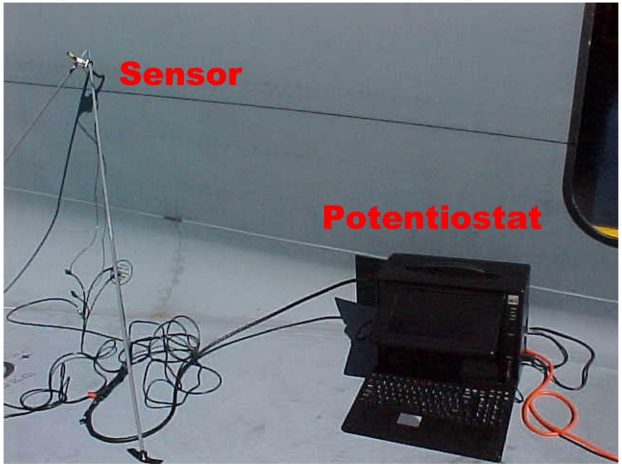

Figure 3. Handheld sensor and portable potentiostat being used to inspect coatings on a KC135 aircraft.[17]

sensitive adhesives.

Based on these ongoing efforts, a multifunctional fluoropolymer wallpaper system with embedded revolutionary corrosion inhibiting and detection features has been developed to address corrosion problems on marine surfaces. One of the present drawbacks of the current appliqué technology is the inability to prevent corrosive elements (e.g., chloride ion) from reaching the substrate where the appliqué is gouged, torn away, or along seams and edges and to give warning if this occurs.

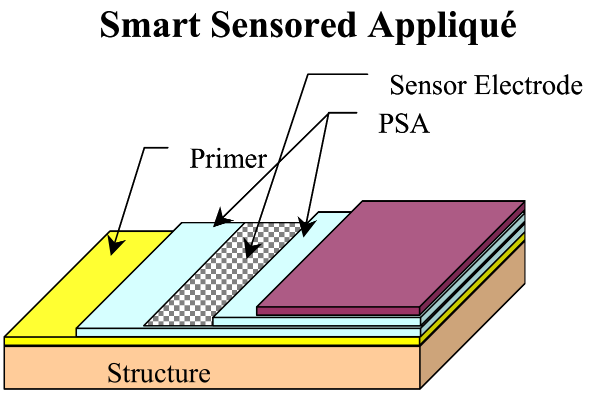

Figure 4. Schematic representation of the smart appliqué showing the embedded sensor electrode.

In addition to the above advantages of directly incorporating corrosion sensors into the appliqué system, the appliqué system itself offers significant advantages over current paint systems. For example, appliqués in general are self-sealing, forming an almost complete vapor barrier. They can be applied quickly; patching may take an hour, while ordinary paint takes 24 hours to cure. In tests so far at Patuxent River, workers have demonstrated that mending a section of a laminated plane can be performed at a rate 44 percent faster than time needed to fix a painted plane.

Furthermore, paint/depaint procedures have been estimated to be responsible for up to 90% of all hazardous waste generated in an aircraft's lifetime.[18] For example, the Naval Aviation Depot (NADEP) discharges an estimated 30 tons of VOCs each year from coating operations. The Army's coating operations have been documented to generate 2,700 tons of hazardous waste. The use of appliqués will eliminate the majority of this hazardous waste.

Advantages of smart appliqué systems over current paint coatings include:

- The ability to apply the appliqué just about anywhere using hand-applied methods in an open environment without the need for a respirator.
- Appliqué removal using hot, high-pressure water, resulting in non-hazardous waste.
- Minimization of cleanup costs with concurrent elimination of most hazardous materials resulting in a reduction of air emissions, wastewater generation, and hazardous waste disposal.
- Excellent adhesion and flexibility so that strains, vibration, and shock will not crack film and allow corrosion.
- Dual-use capability that is easily transferable to other military and commercial vehicles, vessels, and component structures.
- Elimination of "weight creep" resulting from repair-related overpainting of the standard 6- to 12-mil military paint coat, that weighs about 90 lb.
- Appliqué shapes that can be stored on a computer and cut from flat film 'on demand' using a plotter/cutter, when recoating a surface.
- Health monitoring is possible to alert an inspector if the appliqué has been breached or otherwise damaged and corrosion is occurring beneath the film.
- Multifunctional capabilities, including non-stick/anti-graffiti surfaces, lightning strike protection, camouflage, thermal reflectivity, and secondary containment.

EXPERIMENTAL PROCEDURE

Aluminum and steel panels were prepared using MIL-P-24441 type IV epoxy-polyamide primer and appliqués with embedded corrosion sensors. They underwent salt fog exposure (ASTM B117). The principal variables included: substrate material (steel and aluminum), sensor electrode material (aluminum and copper), pressure sensitive adhesive (with and without an organic corrosion inhibitor), appliqué film material (polyvinylidene fluoride, PVDF; polyethylene chlorotrifluoroethylene, ECTFE; and polyperfluoromethyl vinyl ether, MFA). An appliqué without the embedded sensor was used to protect the back and edges of the specimens. Thus the sensing area was limited to the front surface.

One set of specimens consisted of intact appliqués, such as those in a field application. These specimens were not expected to corrode in 2000 hours of salt fog and did not. Other specimens had deliberate defects intended to allow corrosion in this period. In one set, the front appliqué (with sensor) was scribed to the metal. In the other set, a hole was drilled from the backside to allow salt and moisture ingress below the intact front appliqué. Photographs of a specimen with a clear appliqué to show the mesh sensor electrode underneath and of the specimens in the salt fog chamber are given in Figure 5.

Periodically during the exposure, the specimens were removed from the salt fog chamber and EIS measurements were taken using the embedded sensor electrode and a handheld sensor probe on the top of the appliqué. For this later measurement, conditions were chosen so that the intact area of the appliqué was inspected without any impact of the intentional defects. Accordingly, it was useful in evaluating the effectiveness of the different fluoropolymers.

Figure 5. Left) Representative specimen with clear appliqué showing sensor electrode underneath. Right) Specimens in salt fog.

RESULTS AND DISCUSSION

No corrosion is seen in the no-defect specimens following 2000 hours of salt fog exposure. For two of them, the appliqué was removed to check underneath; no corrosion was observed (Figure 6). Small amounts of corrosion were seen at some of the back holes, but not in others. Moisture ingress via the hole was also detected in some specimens between the appliqué and primer. Rust streaks were observed from the scribed steel specimens; minimal corrosion was seen on the scribed aluminum specimens with the exception of the Cu electrode/no corrosion inhibitor specimen discussed below.

Figure 6. Example of no-defect steel specimens before and after appliqué removal.

Even with the scribe, there was little undercutting and corrosion below the appliqué (Figure 7). For aluminum panels, the undercutting was less than 1 mm with the exception of the copper electrode/no corrosion inhibitor specimen where there is evidence of galvanic attack of the aluminum at the bottom of the scribe where water accumulated. In the case where the corrosion inhibitor was incorporated into the adhesive, there was no galvanic corrosion. Corrosion of steel panels after 2000 hours of salt fog ranged from less than 1 mm to ~2 mm. The Cu electrode appliqués appeared to allow more undercutting than the Al electrode appliqués and the adhesive without corrosion inhibitor appeared to allow more undercutting than that with inhibitor.

Typical impedance spectra for the no-defect, back-defect, and scribed specimens are given in Figure 8. Initially, the low frequency impedance in each case is approximately 10^9 Ω, which is excellent for a primer. Upon exposure to the salt fog environment, the impedance of the scribed specimen drops immediately by several orders of magnitude reflecting the breach in the appliqué and primer and ingress of

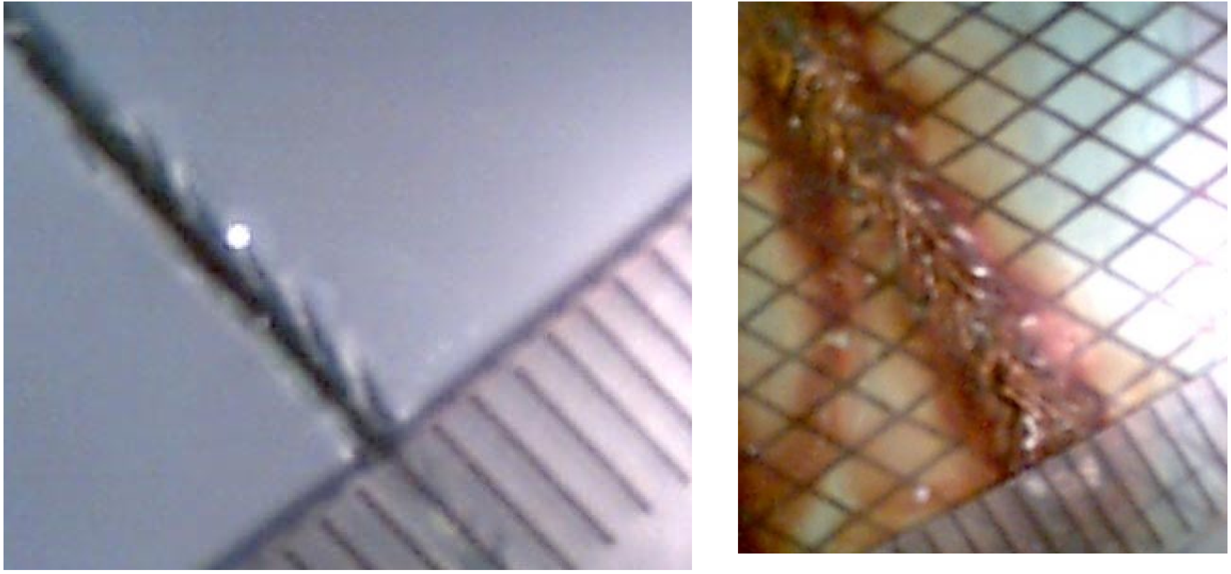

Figure 7. Micrographs of the scribe following 2000 hours of salt fog. Left: Al substrate/copper electrode/corrosion inhibitor – no undercutting of scribe. Right: Steel substrate/copper electrode/no corrosion inhibitor – most severe case of rusting. Shown is the bottom end of the scribe.

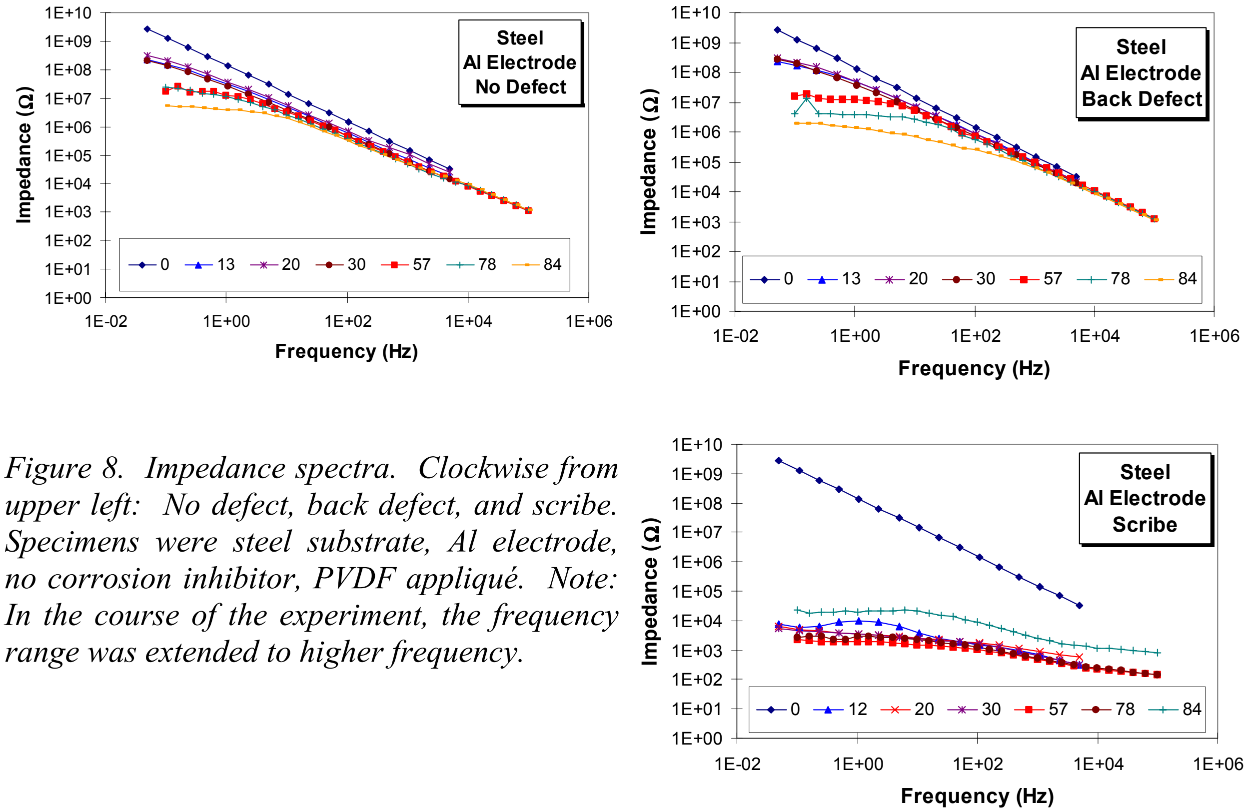

Figure 8. Impedance spectra. Clockwise from upper left: No defect, back defect, and scribe. Specimens were steel substrate, Al electrode, no corrosion inhibitor, PVDF appliqué. Note: In the course of the experiment, the frequency range was extended to higher frequency.

moisture to the substrate. Thus the sensors have a very clear indication of appliqué defect as might be caused by a gouge or other mechanical damage. The other two specimens with the intact sensing appliqué only slowly decrease in impedance with time with the back defect specimen showing a slightly greater decrease. The relative decreases in low frequency impedance for the different conditions are best illustrated by average over all examples of a given defect. The low frequency impedance is given as a function of time in Figure 9. The no defect specimens show a gradual decrease in the impedance over time from 10^9 Ω to ~10^7 Ω; in contrast the scribed specimen shows an immediate drop in impedance to 10^3-10^4 Ω as moisture reaches the substrate. It should be noted that no visible signs of corrosion were apparent at this time.

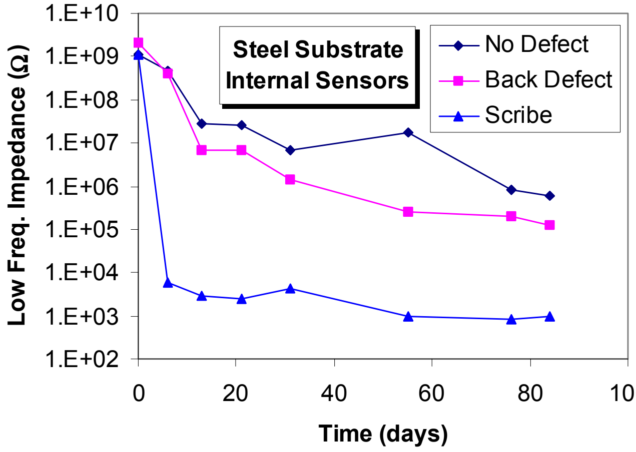

Figure 9. Low frequency impedance as a function of time for no defect, back defect, and scribed steel specimens. The data are averaged over electrode (copper or aluminum) and adhesive (corrosion inhibitor or no corrosion inhibitor).

The back defect specimens exhibited impedances intermediate between the two extremes. These specimens showed the greatest specimen-to-specimen variability both in impedance and appearance as shown in Figure 10. The impedance correlated well with the presence or absence of corrosion at the end of the test. The three specimens with impedance approximately 10^{-5} Ω had visible corrosion products while the one with the highest impedance did not have visible signs of corrosion.

Handheld sensor measurements were also taken to track any degradation of the appliqué itself (the measurements shown above pertained to the primer below the appliqué). The primer would be expected to show signs of degradation before the appliqué would so it serves as an early warning. Measurements of the no-defect specimens, averaged over each of the three film chemistries, are shown in Figure 11. The impedance remains high for each film with no significant difference between them, indicating excellent corrosion protection with no degradation – a finding supported by the photographs and the internal sensor measurements.

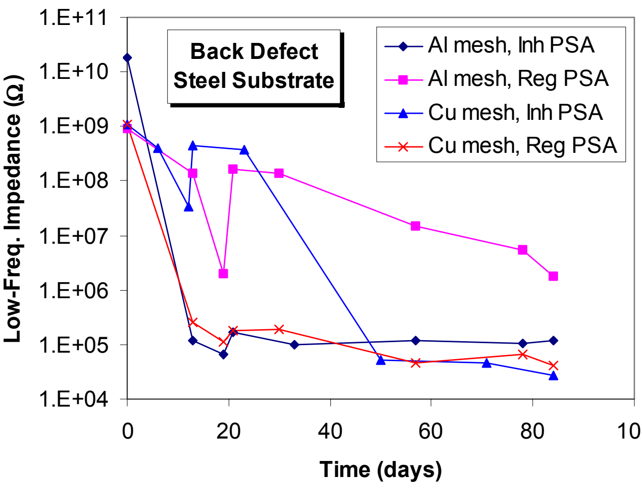

Figure 10. Low-frequency impedance of the steel specimens with a back defect.

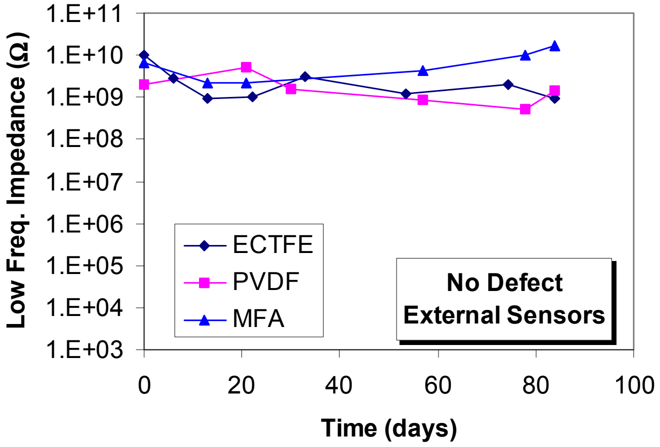

Figure 11. Low-frequency impedance as a function of salt fog exposure averaged over the three film chemistries. The data were acquired with an external hand-held sensor to inspect the appliqué itself.

CONCLUSIONS

The conclusions of the project can be summarized as follows:

- The appliqués provide excellent corrosion protection.
- The embedded sensor electrodes enable detection of appliqué defects and health monitoring.
- There was no apparent difference in performance of the three fluoropolymers in the salt fog test.
- The simple low-frequency impedance measurement was as effective as the more complex equivalent circuit modeling in monitoring appliqué health.
- Both aluminum and copper sensor electrodes were equally effective although the copper electrode might promote galvanic corrosion of the aluminum substrate.
- The corrosion inhibitor incorporated into the adhesive prevents galvanic attack of the aluminum substrate by the copper electrode and may reduce corrosion at a scribe.
- Electrical connection to the sensor electrodes was easily achieved through the pressure sensitive adhesive.

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