

Corrosion Protection and Health Monitoring by Smart Appliqués

Guy D. Davis
DACCO SCI, INC.
10260 Old Columbia Road
Columbia, MD 21046
davis@daccosci.com

Andrew W. Dalgleish
Integument Technologies, Inc.
70 Pearce Avenue
Tonawanda, NY 14150

Terry G. Vargo
Integument Technologies, Inc.
70 Pearce Avenue
Tonawanda, NY 14150

Douglas Deason
U.S. Army Space and Missile Defense
Command
Bldg 5220
Redstone Arsenal, AL 35898

ABSTRACT

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. The tropical marine environment, such as the Marshall Islands or the Hawaiian Islands, 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 except when a copper electrode induced galvanic attack. 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 such as the Kwajalein Atoll in the Marshall Islands and the Pacific Missile Range Facility at Kauai, Hawaii. These facilities include 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. Remoteness of facilities further exacerbates the situation by limiting the staff available to perform frequent maintenance of structures and systems. As an example of the aggressive environment, corrosion made a half-million-dollar boom truck unsafe and useless at Kwajalein Atoll after only 3 years. The constant salt 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. However, 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).

Paintless application of films using pressure sensitive “peel and stick” adhesive technology is another corrosion mitigation approach. Although appliqués provide excellent barriers and 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, for very critical structures, there is a need to have a smart, sensed appliqué whose health can be monitored with appropriate instrumentation. Such procedures would enable condition-based maintenance (CBM), increase system reliability, and decrease cost.

A smart appliqué not only is very effective in providing corrosion protection, but also is capable of health monitoring for condition-based maintenance by building a real-time corrosion sensor directly into a peel and stick coating system. 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 the results of accelerated laboratory testing. The appliqué coating system:

- Is very protective against corrosion
- Involves no VOC emissions during application
- Can have 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 previously 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 appliqué, have demonstrated high performance levels for protection from severe chemical, temperature and other corrosive environments.²⁻⁴

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.⁵⁻⁹ 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. Potentiostats on a chip are also being developed that would reduce the cost and complexity of a full-powered potentiostat, but would be suitable for the smart appliqué. Inspection of exterior surfaces and accessible interior surfaces is achievable using a portable handheld sensor. Permanent sensors can be used for less accessible areas where a single wire and a ground connection allow data acquisition at a convenient point.

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 along seams and edges or where the appliqué is gouged or torn away and to give warning if this occurs. To address this issue, a multifunctional fluoropolymer wallpaper system has been developed with a corrosion inhibitor in the pressure sensitive adhesive (PSA) and a corrosion sensor, consisting of a metal mesh or expanded metal foil, added between two layers of adhesives as shown in Figure 1.

In addition to directly incorporating corrosion sensors into the appliqué system, the appliqué system itself offers other 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. Tests at Naval Air Systems Command Patuxent River have shown that mending a section of an appliquéed plane can be achieved in approximately half the time needed to fix a painted plane.¹⁰

Furthermore, paint/depaint procedures have been estimated to be responsible for up to 90% of all hazardous waste generated in an aircraft's lifetime.¹¹ For example, the Naval Aviation Depot (NADEP)

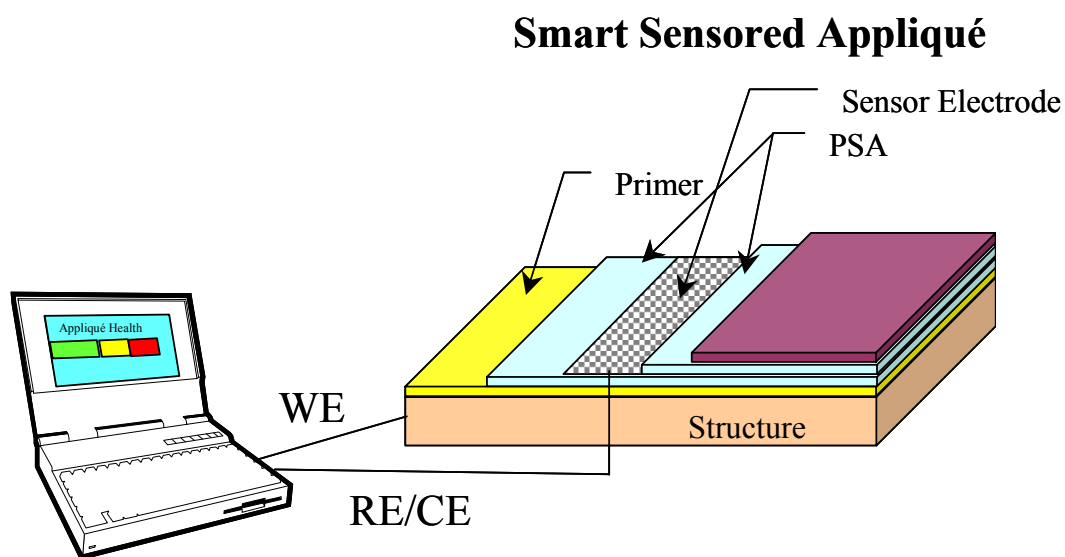


Figure 1. Schematic representation of the smart appliqué showing the embedded sensor electrode. The potentiostat is shown as a portable computer with the working electrode (WE) connected to the substrate and the reference and counter electrodes (RE/CE) connected to the sensor electrode.

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.

EXPERIMENTAL PROCEDURE

Aluminum (3105) and cold rolled steel (1008) 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). Table 1 lists the experimental matrix of specimens. 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 through the panel and the back appliqué prior to applying the front appliqué to allow salt and moisture ingress below the intact front appliqué.

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.

Table 1. Experimental Matrix

Substrate	Electrode	Inhibitor	Polymer	Defect
Steel	Al	yes	ECTFE	none
Steel	Al	yes	ECTFE	scribe
Steel	Al	yes	ECTFE	back hole
Steel	Al	no	PVDF	none
Steel	Al	no	PVDF	scribe
Steel	Al	no	PVDF	back hole
Steel	Cu	yes	ECTFE	none
Steel	Cu	yes	ECTFE	scribe
Steel	Cu	yes	ECTFE	back hole
Steel	Cu	no	MFA	none
Steel	Cu	no	MFA	scribe
Steel	Cu	no	MFA	back hole
Aluminum	Al	yes	ECTFE	none
Aluminum	Al	yes	ECTFE	scribe
Aluminum	Al	yes	ECTFE	back hole
Aluminum	Al	no	PVDF	none
Aluminum	Al	no	PVDF	scribe
Aluminum	Al	no	PVDF	back hole
Aluminum	Cu	yes	ECTFE	none
Aluminum	Cu	yes	ECTFE	scribe
Aluminum	Cu	yes	ECTFE	back hole
Aluminum	Cu	no	MFA	none
Aluminum	Cu	no	MFA	scribe
Aluminum	Cu	no	MFA	back hole

RESULTS AND DISCUSSION

No corrosion was 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 2). 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 copper electrode/no corrosion inhibitor specimen discussed below.

Even with the scribe, there was little undercutting and corrosion below the appliqué. For aluminum panels, the undercutting was less than 1 mm with the exception of the copper electrode/no corrosion inhibitor specimen where there was 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 undercutting at the scribe. The copper-electrode appliqué appeared to allow more undercutting than the aluminum electrode appliqué and the adhesive without corrosion inhibitor appeared to allow more undercutting than that with inhibitor. However, the differences were slight.

Typical impedance spectra for the no-defect, back-defect, and scribed steel specimens are given in Figure 3. Initially, the low frequency impedance in each case is approximately $10^9 \Omega$, which is excellent



Figure 2. Example of no-defect steel specimens after appliqué removal.

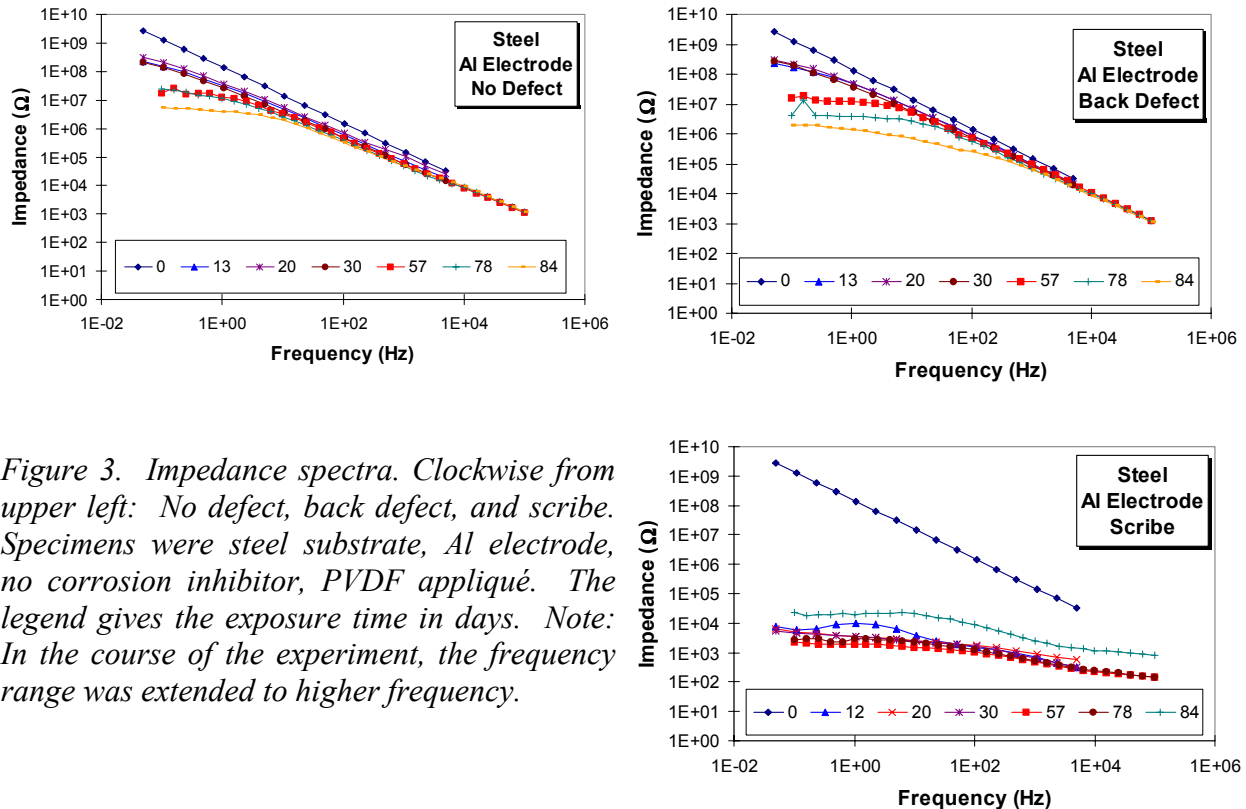


Figure 3. Impedance spectra. Clockwise from upper left: No defect, back defect, and scribe. Specimens were steel substrate, Al electrode, no corrosion inhibitor, PVDF appliqué. The legend gives the exposure time in days. Note: In the course of the experiment, the frequency range was extended to higher frequency.

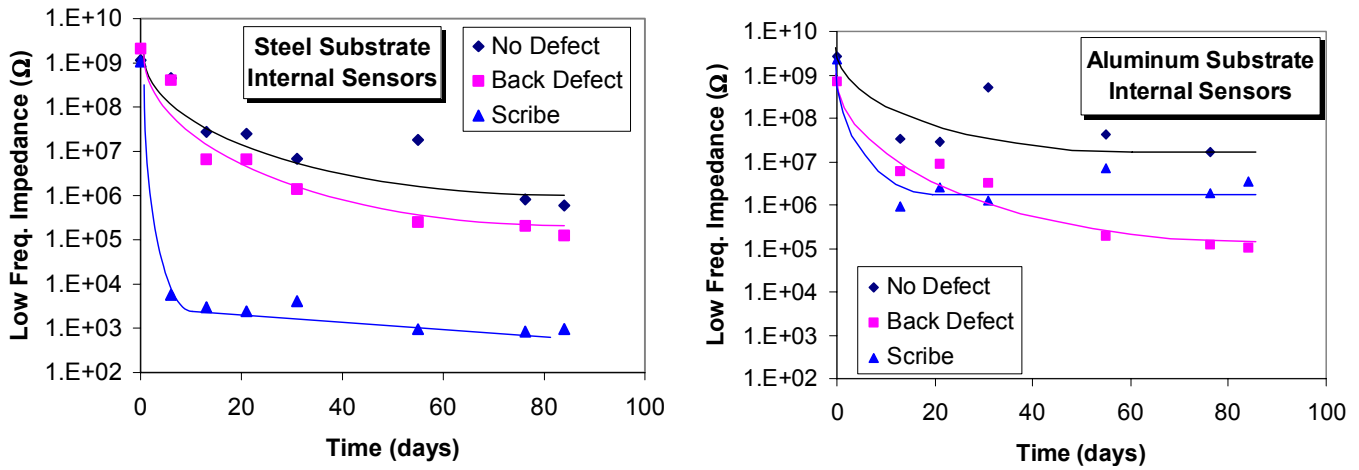


Figure 4. Low frequency impedance as a function of time for no defect, back defect, and scribed specimens. Left: Steel. Right: Aluminum. The data are averaged over electrode (copper or aluminum) and adhesive (corrosion inhibitor or no corrosion inhibitor).

for a primer. Upon exposure to salt fog, the impedance of the scribed specimen dropped immediately by several orders of magnitude reflecting the breach in the appliqué and primer and initiation of substrate corrosion. 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 (no defect and back defect) 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 4. The no defect specimens showed a gradual decrease in the impedance over time from $10^9 \Omega$ to $\sim 10^7 \Omega$. In contrast the scribed steel specimens showed an immediate drop in impedance to 10^3 - $10^4 \Omega$ as corrosion at the scribe began while the scribed aluminum specimens show a lesser average drop to $10^6 \Omega$ in the same time, similar to that of the back defect specimens. The

average higher impedance is likely a measure of a passive film protecting the aluminum; little or no corrosion was seen at the aluminum scribe, but there was significant difference between specimens. The copper electrode / no corrosion inhibitor specimen which exhibited the galvanic corrosion mentioned above also exhibited a very low impedance, similar to that of the scribed steel specimens, reflecting the initiation of corrosion (Figure 5). It should be noted that no visible signs of corrosion were apparent when the impedance first dropped. With the addition of the corrosion inhibitor in the adhesive, no corrosion was visible and the low-frequency impedance remained high. (The drop in impedance at 12 days might reflect damage to the passive film or may be an errant point.)

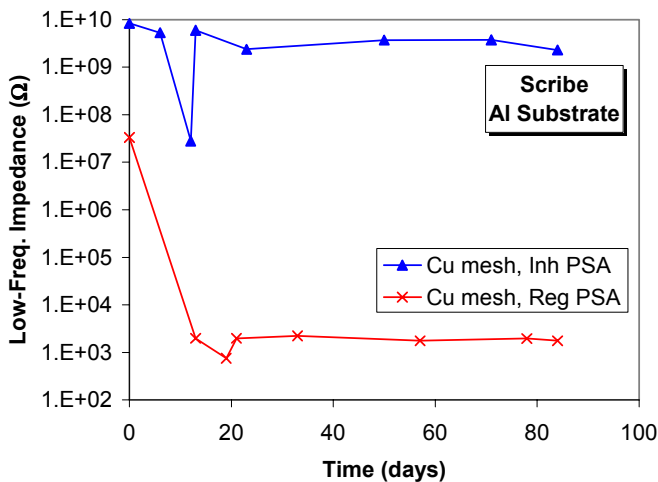


Figure 5. Low-frequency impedance as a function of time for an aluminum substrate with copper mesh: with and without a corrosion inhibitor in the adhesive.

The back defect steel 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 6. The impedance correlated well with the presence or absence of corrosion at the end of the test. The three specimens with impedance approximately $10^5 \Omega$ had visible corrosion products while the one with the highest impedance did not have visible signs of corrosion.

Aside from the galvanic attack of the aluminum by the copper mesh, there was little difference in results using the copper or aluminum mesh, either in appearance or sensor measurements. Figure 7 shows virtually identical low-frequency impedance results for the two meshes.

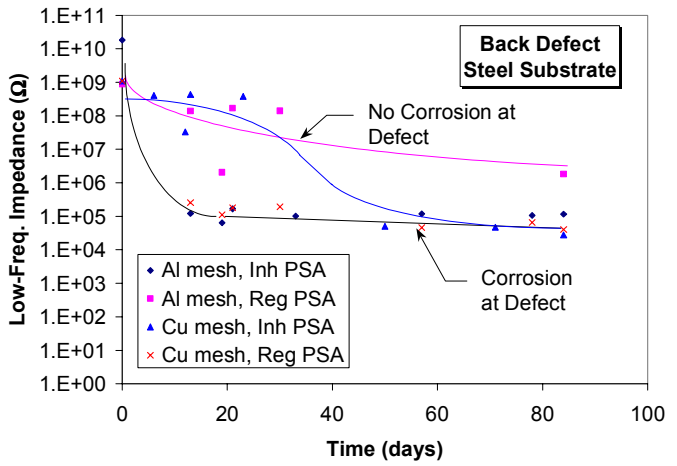


Figure 6. Low-frequency impedance of the steel specimens with a back defect.

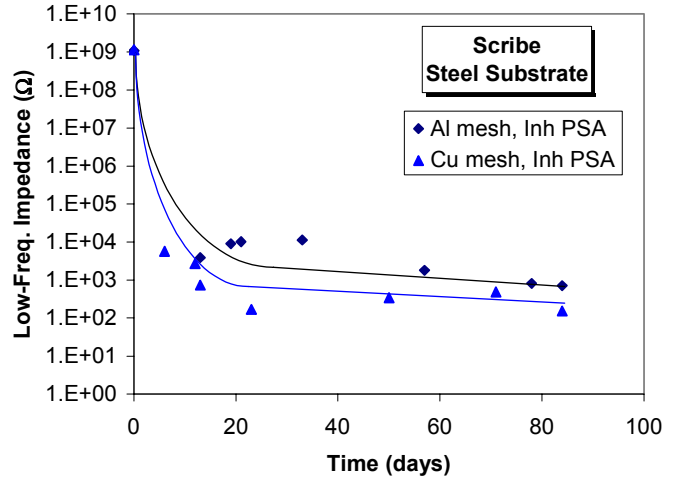
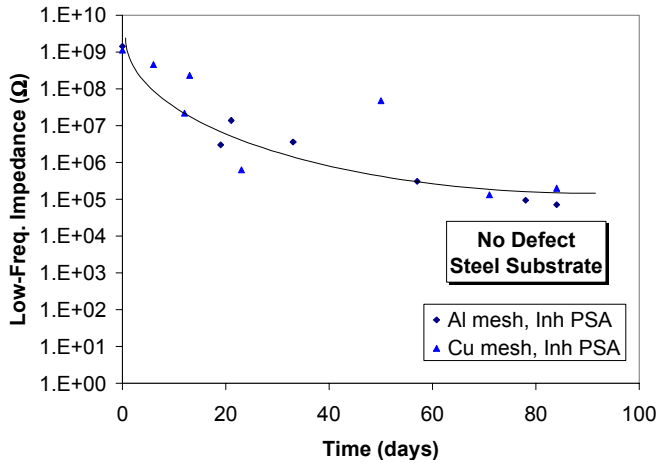


Figure 7. Comparison of aluminum and copper meshes: steel substrate, adhesive with inhibitor. Left: No defect specimens. Right: Scribed specimens.

Handheld sensor measurements were also taken to track any degradation of the appliqué itself. Measurements of the no-defect specimens, averaged over each of the three film chemistries, are shown in Figure 8. The impedance measurement is dominated by the lowest impedance path in the case where parallel pathways for current are present. In the case of the handheld sensor, the topcoat and primer are in series and the impedance measurement is dominated by the higher impedance of the topcoat. The impedance remained 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. Comparison of the results from Figure 4 and Figure 8 suggests that the decrease in the primer impedance observed by the internal sensor is likely caused by moisture ingress from the edges of the appliqué. For these small specimens, no point is more than 5 cm from an edge. Moisture intrusion at the edge can give early warning of potential corrosion. In cases of immersion or very severe service, edges can be sealed to eliminate this source of moisture.

Based on these laboratory results, a demonstration is underway at the Pacific Missile Range Facility in Kauai, Hawaii. Steel panels with smart appliqué have been placed on an exposure rack and will periodically be inspected using EIS to compare performance with similar panels in laboratory accelerated testing. Other appliqué, without the embedded sensors, have been applied to several structures for visual comparison with surrounding painted areas (Figure 9).

CONCLUSIONS

The conclusions of the project can be summarized as follows:

- The appliqué 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.
- 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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REFERENCES

¹ Gerhardus H. Koch, Michiel P.H. Brongers, Neil G. Thompson, Y. Paul Virmani, Joe H. Payer, "Corrosion Costs and Preventive Strategies in the United States," Report by CC Technologies Laboratories, Inc. to Federal Highway Administration (FHWA), Office of Infrastructure Research and Development, Report FHWA-RD-01-156, September 2001.

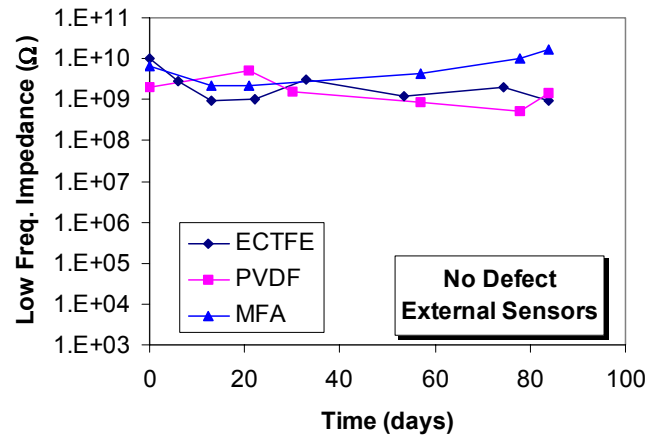


Figure 8. Low-frequency impedance as a function of salt fog exposure averaged over the three film chemistries. The data were acquired with an external hand-held sensor to inspect the appliqué itself.



Figure 9. Application of appliqué on tank at Pacific Missile Range Facility.

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- ² Holdsworth, G. S., and Dalglish, A. W., "Plasma Advancement Expands Applications of Fluoropolymer Coatings and Linings," *Materials Performance*, **40**(9), 32 (2001).
- ³ Kaplan, S. L. and Naab, D. J., "PSA's Tenaciously Bond to Non-stick Film After Plasma Treatment", *Adhesives & Sealants Industry*, February 2001, pp. 40-42.
- ⁴ "And the Winners Are...: Honoring the Chemical Industry's 'VIPs – very innovative products,'" *Chemical Processing* November 2001, pp. 37.
- ⁵ G.D. Davis, C.M. Dacres, and L.A. Krebs, "In-Situ Corrosion Sensor for Coating Testing and Screening," *Materials Performance* **39**(2), 46 (2000).
- ⁶ G.D. Davis, C.M. Dacres, and L.A. Krebs, "EIS-Based In-Situ Sensor for the Early Detection of Coating Degradation and Substrate Corrosion," *Corrosion2000*, Paper 275 (NACE, Houston, TX, 2000).
- ⁷ L.A. Krebs, G.D. Davis, and C.M. Dacres, "Monitoring Moisture Intrusion and Coating Degradation in the Field," *Corrosion2001*, Paper 1430 (NACE, Houston, TX, 2001).
- ⁸ G.D. Davis, L.A. Krebs, and C.M. Dacres, "Coating Evaluation and Validation of Accelerated Test Conditions Using an In-Situ Corrosion Sensor, *J. Coatings Technol.* **74**(935), 69 (December 2002).
- ⁹ G.D. Davis and C.M. Dacres, "Electrochemical Sensors for Evaluating Corrosion and Adhesion on Painted Metal Structures," U.S. Patent 5,859,537; "Portable Hand-Held In-Situ Electrochemical Sensor for Evaluating Corrosion and Adhesion on coated and Uncoated Metal Substrates," U.S. Patent 6,054,038; "In-Situ Electrochemical-Based Moisture Sensor for Detecting Moisture in Composite and Bonded Structures," U.S. Patent 6,313,646; G.D. Davis, C.M. Dacres, and L.A. Krebs, "An Adhesive Tape Sensor for Detecting and Evaluating Coating and Substrate Degradation Utilizing Electrochemical Processes," U.S. Patent 6,328,878.
- ¹⁰ John Wenke, Appliqué Initiative Review, AIRLANT (March 26, 1999), unpublished.
- ¹¹ P. Proctor, "Boeing, 3M Envision Paintless JSF," *Aviation Week and Space Technology*, p.72, June 9, 1997