Corrosion Protection and Condition Monitoring Using 'Smart' Appliqués

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The tropical marine environment is highly corrosive, and improved corrosion protection and control methods are needed to protect assets and infrastructure subjected to it. One solution to this problem is the "smart" appliqué. The technology, a peel-and-stick fluoropolymer film with a sensor electrode and pressure-sensitive adhesive, provides corrosion protection and condition monitoring to alert an inspector if the appliqué has been damaged or has deteriorated. Electrochemical impedance spectroscopy measurements using the embedded sensors allow condition monitoring. The sensors can detect poor appliqué installation or damage to the appliqué before any damage to the structure occurs.

Corrosion of test assets and other structures used by the U.S. Department of Defense (DoD) Missile Defense Agency (MDA) (Arlington, Virginia) and other DoD branches is an ongoing maintenance and reliability issue. Corrosion costs the DoD an estimated $20 billion per year—the greatest factor in life-cycle costs.[1] The cost of repairs, maintenance, and replacement is a direct cost. Injuries and the loss of readiness are additional indirect costs, which cannot be assessed in dollar amounts—especially during a national emergency or wartime.

Corrosion is aggravated by the need to operate in some very corrosive environments. For example, MDA has test assets at remote locations at the Kwajalein Atoll in the Marshall Islands in the Pacific Ocean (Figure 1[2]). Critical test assets include radars as well as civil and base infrastructure (buildings, water and fuel systems, and power plants). Such marine locations, especially those in hot climates, are particularly corrosive. The entire island is exposed to a nearly continuous saltwater mist. The facilities' remoteness further exacerbates the situation by limiting the staff available to perform frequent maintenance.

The corrosiveness of the tropical environment is exemplified by a $500,000 boom truck that corrosion made unsafe and useless at Kwajalein Atoll after only 3 years of operation. The constant salt spray from the Pacific corrodes all structures and equipment, dramatically reduces operational lifetime, and increases life-cycle costs.

The most common approach to preventing corrosion of metallic structures is applying protective coatings. Paints can be very effective, but 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 may involve environmental issues of waste from old paint (lead, chromates) and volatile organic compounds. Furthermore, the presence of a virtually continuous salt spray creates a situation in which the surface becomes recontaminated. Thus, repaired and painted areas require frequent treatment over short periods. Numerous approaches have been attempted, but a long-term solution has been elusive.

To minimize coating maintenance, there have been significant efforts to modify or develop paint systems to comply with ever-increasing air quality and human protection demands. Parallel efforts have demonstrated that paintless application of films using pressure-sensitive "peel-and-stick" (appliqué) adhesive technology is another corrosion mitigation approach that is gaining momentum.[3-5]

Appliqués have proven to be very successful. Corrosion can occur under the film, however. Improper film installation or moisture intrusion through compromised sections of the film also can cause corrosion. Consequently, there is a need for a smart, sensored appliqué whose condition can be monitored with appropriate instrumentation. Such a technology would enable condition-based maintenance, increase system reliability, and decrease cost. The sensored 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.

Several fluoropolymer-based, paintless corrosion protection systems have been developed in the past several years for applications in the chemical and food processing and transportation industries. The appliqués have demonstrated high performance levels for protection from severe chemical, temperature, and other corrosive environments.

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.[6-9] The sensor, when coupled with a portable potentiostat, is suitable for both laboratory and field inspection. The "smart" appliqué is illustrated in Figure 2. Here a metal mesh or expanded metal foil is added to the appliqué between two layers of pressure-sensitive adhesives. The smart appliqué thus acts as a sensor electrode.

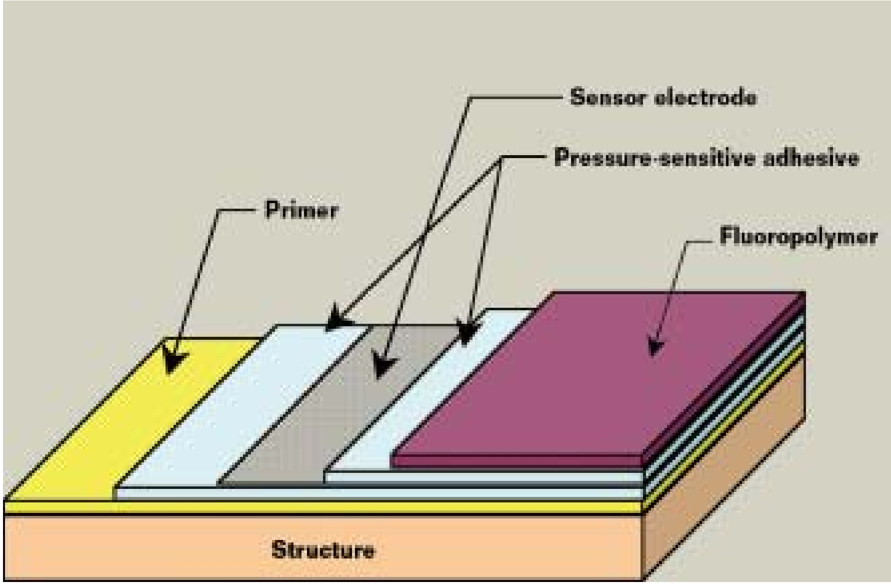
The smart appliqué system itself offers the following advantages:

- Excellent corrosion protection capabilities
- Hand application in an open environment without the need for a respirator
- Self-sealing capabilities, forming an almost complete vapor barrier. Appliqués can be applied quickly; patching may take an hour. An appliquéd surface can be repaired more rapidly than a painted one.
- Minimal cleanup costs with concurrent elimination of most hazardous

FIGURE 1

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 wind blocking. U.S. Army photo.

FIGURE 2



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

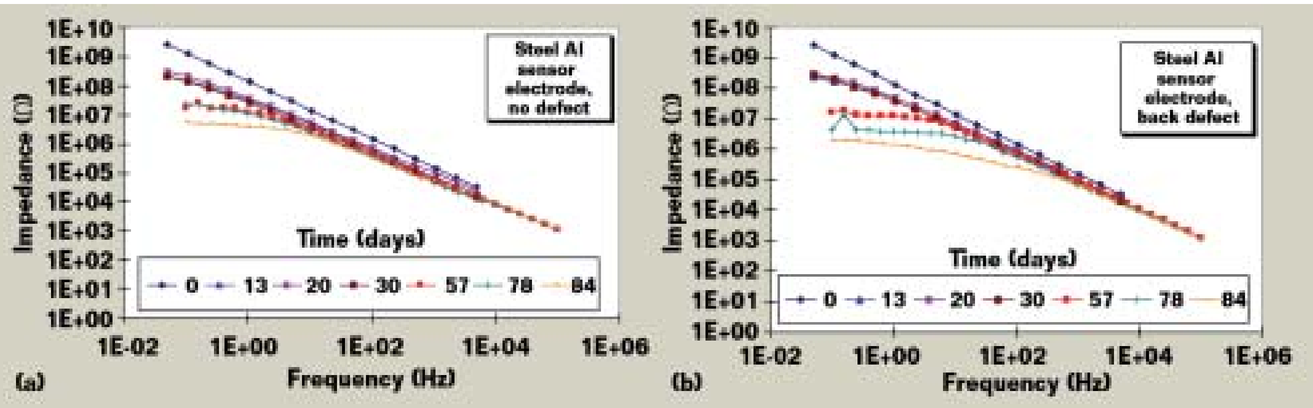
FIGURE 3

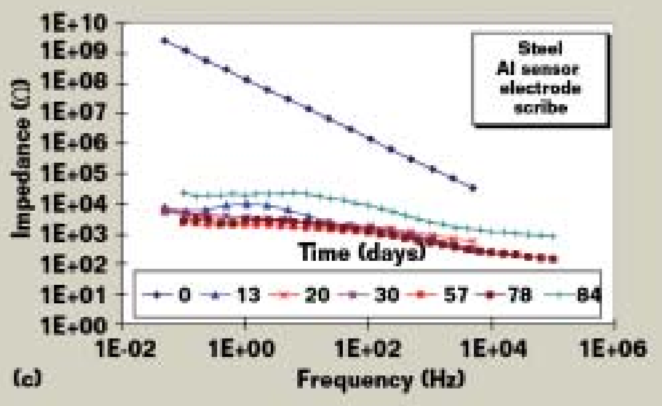
Example of steel specimens after salt fog exposure before and after removal of no-defect appliqué.

materials, yielding reduced air emissions, wastewater generation, and hazardous waste disposal

- Excellent adhesion and flexibility so that strains, vibration, and shock will not crack the film and allow corrosion
- Removal using hot, high-pressure water, yielding nonhazardous waste
- Elimination of "weight creep" from repair-related overpainting of the standard 6- to 12-mil (150- to 300-μm) military paint coat
- Appliqué shapes that can be stored on a computer and cut from flat film "on-demand," using a plotter/cutter when recoating a surface
- Condition monitoring to alert an inspector if the appliqué has been breached or otherwise damaged and corrosion is occurring beneath the film

FIGURE 4





Impedance spectra. Specimens were steel substrate, Al sensor electrode, no corrosion inhibitor, PVDF appliqué. Note: In the course of the experiment, the frequency range was extended to higher frequencies. (a) No defect, (b) back defect, (c) scribe.

• Multifunctionality capabilities, including nonstick/antigraffiti surfaces, lightning strike protection, electromagnetic interference (EMI) and ultraviolet shielding, thermal reflectivity, chemical agent resistance, camouflage, and secondary containment.

Experimental Procedures

Aluminum and steel panels were prepared using MIL-P-24441 type IV epoxy-polyamide primer and appliqués with embedded corrosion sensors. The panels underwent 2,000 h of salt fog exposure (ASTM B117[10]). Both steel and aluminum substrates were protected with three smart appliqué film materials: 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. As expected, these specimens did not corrode in 2,000 h of salt fog exposure. Other specimens had deliberate defects intended to facilitate corrosion within this period. In one set, the front appliqué 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.

Periodically, electrochemical impedance spectroscopy measurements were taken using the embedded sensor electrode and a handheld sensor probe on the top of the appliqué. For the latter measurement, conditions were chosen so that the intact area of the appliqué was inspected without altering the intentional defects. Accordingly, these conditions provided a useful environment for evaluating the effectiveness of the different fluoropolymers.

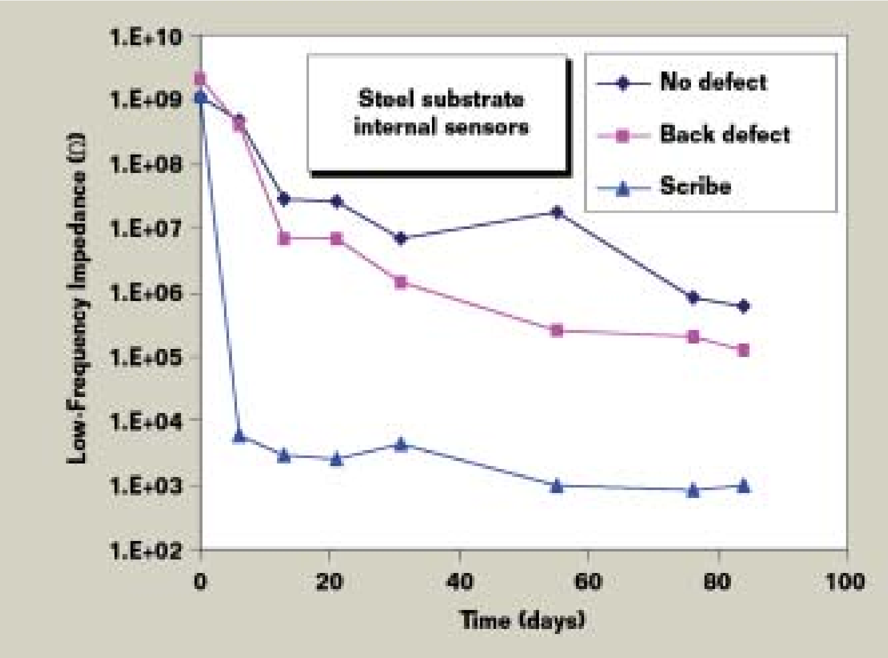
Results and Discussion

The authors observed no corrosion in the no-defect specimens, including those from which the appliqué was removed to check the underside (Figure 3). Small amounts of corrosion were seen at some of the back holes but not in others. Moisture ingress via the hole also was 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.

Even with the scribe, there was little undercutting and corrosion below the appliqué. For aluminum panels, the undercutting was <0.04 in. (1 mm). Corrosion of steel panels after 2,000 h of salt fog exposure ranged from <0.04 to ~0.08 in. (2 mm).

Figure 4 shows typical impedance spectra for the no-defect, back-defect, and scribed specimens. Initially, the low-frequency impedance in each case is approximately $10^9\ \Omega$—excellent for a primer. Upon exposure to the salt fog environment, the impedance of the scribed specimen drops immediately by several orders of magnitude; this reflects the breach in the appliqué and primer and ingress of moisture to the substrate. Hence 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 or smart appliqué decrease in impedance only slowly 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 averaging over all examples of a given defect.

FIGURE 5

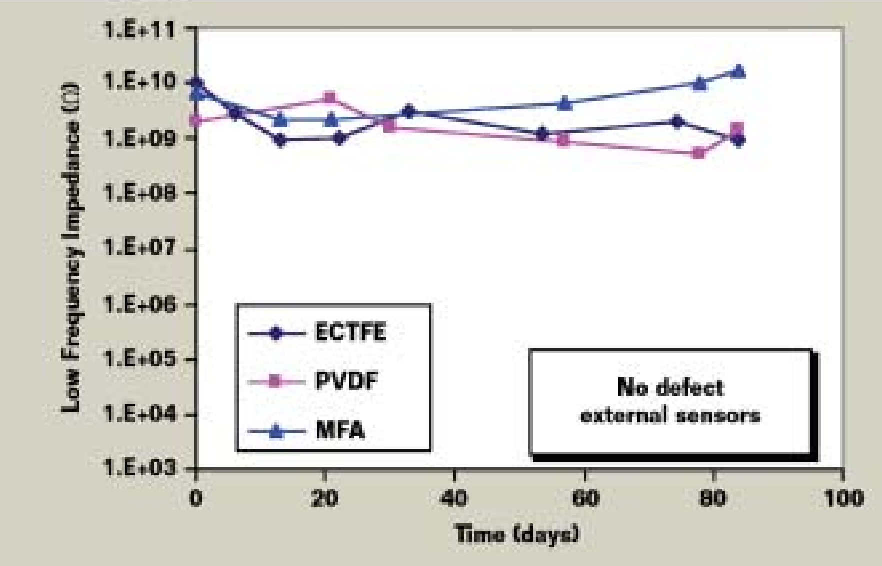


Low-frequency impedance as a function of time for no-defect, back-defect, and scribed-steel specimens. The data are averaged over sensor electrode (copper or aluminum) and adhesive (corrosion inhibitor or no corrosion inhibitor).

Figure 5 gives the low-frequency impedance as a function of time. The no-defect specimens show a gradual decrease in the impedance over time from $10^9\ \Omega$ to ~$10^7\ \Omega$. In contrast, the scribed specimen shows an immediate drop in impedance to $10^3\ \Omega$ to $10^4\ \Omega$ as moisture reaches the substrate. Note that no visible signs of corrosion were apparent at this time.

The back-defect specimens exhibited impedances ranging between the two extremes. These specimens showed the greatest specimen-to-specimen variability both in impedance and appearance. The impedance correlated well with the presence or absence of corrosion at the end of the test. The three specimens with imped-

FIGURE 6



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.

ance ~10^{-5} Ω had visible corrosion products; the one with the highest impedance had no visible signs of corrosion.

The investigators also took hand-held sensor measurements to track any degradation of the appliqué itself. The measurements described above pertained to the primer below the appliqué. One would expect the primer to show signs of degradation before the appliqué would, so it serves as an early warning. Figure 6 shows measurements of the no-defect specimens, averaged over each of the three film chemistries. The impedance remains high for each film with no significant difference among them, indicating excellent corrosion protection with no degradation—a finding supported by the photographs and the internal sensor measurements.

Conclusions

The conclusions can be summarized as follows:

- The appliqués provide excellent corrosion protection.
- The embedded sensor enables detection of appliqué defects and condition monitoring.
- The three fluoropolymers each gave equivalent corrosion protection in the salt fog test.

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References

1. G.H. Koch, M.P.H. Brongers, N.G. Thompson, Y.P. Virmani, J.H. Payer, "Corrosion Costs and Preventive Strategies in the United States," U.S. Federal Highway Administration Report FHWA-RD-01-156, September 2001.

2. Ronald Reagan Ballistic Missile Defense Test Site, http//:www.smdc.army.mil/RTS.html.

3. G.S. Holdsworth, A.W. Dalgleish, "Plasma Advancement Expands Applications of Fluoropolymer Coatings and Linings," MP, 40 9 (2001): pp. 32-36.

4. S.L. Kaplan, D.J. Naab, "PSA's Tenaciously Bond to Non-stick Film After Plasma Treatment," Adhesives & Sealants Industry (February 2001): pp. 40-42.

5. "And the Winners Are…: Honoring the Chemical Industry's 'VIPs—Very Innovative Products," Chemical Processing (November 2001): p. 37.

6. G.D. Davis, C.M. Dacres, L.A. Krebs, "In-Situ Corrosion Sensor for Coating Testing and Screening," MP 39, 2 (2000): p. 46.

7. G.D. Davis, C.M. Dacres, L.A. Krebs, "EIS-Based In-Situ Sensor for the Early Detection of Coating Degradation and Substrate Corrosion," CORROSION/2000, paper no. 275 (Houston, TX: NACE, 2000).

8. L.A. Krebs, G.D. Davis, C.M. Dacres, "Monitoring Moisture Intrusion and Coating Degradation in the Field," CORROSION/2001, paper no. 1430 (Houston, TX: NACE, 2001).

9. G.D. Davis, 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. ASTM B117, "Standard Practice for Operating Salt Spray (Fog) Apparatus" (West Conshohocken, PA: ASTM, 1997).

11. P. Proctor, "Boeing, 3M Envision Paintless JSF," Aviation Week and Space Technology (June 9, 1997): p. 72.

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