

Early Detection of Steel Corrosion via “Turn-On” Fluorescence in Smart Epoxy Coatings

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ABSTRACT In the present work, we describe the successful application of spiro[1*H*-isoindole-1,9'-[9*H*]xanthen]-3(2*H*)-one, 3',6'-bis(diethylamino)-2-[(1-methylethylidene)amino] (“FD1”) as a smart indicator in epoxy-based coatings for the early detection of steel corrosion. The FD1 indicator was used for epoxy-based coatings on steel for its desirable property of “turn-on” fluorescence upon forming a complex with ferric ions produced at the anodic site during steel corrosion and because it does not prematurely fluoresce when mixed with the coating precursors (i.e., epoxy resin and amine). This indicator, after incorporation into a filled epoxy coating at a concentration as low as 0.5 wt %, was observed to become fluorescent in areas where corrosion started before any obvious sign of metal damage was observable. FD1 fluorescence was apparent both in areas around a scribed portion of the coating where the metal was exposed and in *undercoating* corrosion, where the coating surface was intact. This nondestructive method of early corrosion detection can help signal when maintenance is needed before the metal suffers serious damage.

KEYWORDS: smart coating • turn-on fluorescence • corrosion detection • steel corrosion • epoxy coating

1. INTRODUCTION

One of the most common approaches to protecting metal surfaces from corrosion is the application of a protective coating. Polymeric coatings are widely used on steel surfaces to help prevent corrosion. However, over time the protective coating can fail because of prolonged exposure to the environment or mechanical damage, leaving portions of the metal surface susceptible to corrosion. Corrosion, if undetected and untreated, can lead to catastrophic metal failure, causing economic and safety consequences.

Polymeric coatings, in addition to their passive protecting and aesthetic functions, are increasingly being designed to serve active roles in response to internal/external stimuli as so-called “smart coatings” (1). One widely studied application of these types of materials is in metal-corrosion protection. Autonomous self-healing films, for example, have received great attention recently (1–3), where physical damage in a coating is self-repaired to recover barrier properties before metal corrosion occurs. Another stimuli-responsive approach is the use of inhibitors incorporated within the coating that are released “on demand” when corrosion occurs (4–7), to effectively halt further damage. The two approaches described above function to extend the useful lifetime of the coating by attempting to prevent or minimize the impact of the corrosion reaction. However, one strategy of particular significance that has not yet been

adequately addressed, especially for epoxy-based coatings on steel, is the ability for a coating to detect and report early-stage metal corrosion before any visible sign of it can be seen. A coating that reports the onset of underlying corrosion could, consequently, signal when maintenance should be performed to prevent further metal damage.

In situ early corrosion detection can be realized by incorporating indicator molecules into coating formulations that detect the onset of corrosion because of their interaction with ions generated during corrosion reactions. As a result of this interaction, the color or fluorescence change of the indicator can be observed or recorded. A simple detection method based on this concept was reported by Zhang and Frankel (8) utilizing pH-sensitive compounds in an acrylic coating applied on an aluminum substrate, which change their color or fluorescence as a result of an increase in the pH at cathodic areas of corrosion. A similar approach was also reported by Calle and Li (4), in which they used pH-responsive microcapsules that release an indicator in polyurethane coatings at the alkaline cathodic area of corrosion.

For steel substrates, however, the most widely used protective coatings are epoxy-based because of their excellent chemical resistance, mechanical strength, and adhesion to metal surfaces. Although the pH-triggered approach seemed to work well in acrylic and polyurethane coating systems, it proves to be very challenging in epoxy coatings. Johnson and Agarwala attempted the use of fluorescein in an epoxy primer coating applied onto an aluminum plate and reported that the indicator became “prematurely fluorescent” in the epoxy coating (9). This phenomenon can be ascribed to the premature chemical reaction between fluo-

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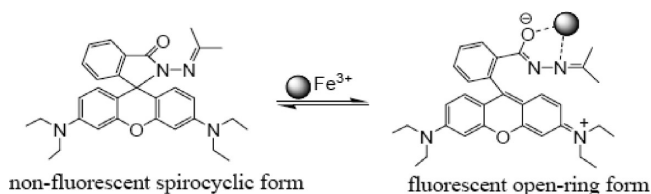


FIGURE 1. CHEF of FD1 upon binding with Fe^{3+} (16).

rescein and one of the coating precursors, the amine-based hardener. If pH-sensitive compounds can be ionized prematurely by coating formulation components, they will not be able to sense corrosion by the same trigger mechanism. Thus, it would be very unlikely to use the pH-sensing approach in epoxy-based coatings for corrosion detection.

An alternative corrosion-sensing approach involves the interaction of an indicator with metal ions liberated during the corrosion reaction, resulting in a change in the fluorescence of the probe. Different compounds have been attempted for corrosion detection with this approach on aluminum substrates (9–12). Although success of various extents was reported in the detection of aluminum corrosion, no success has been reported, to the best of our knowledge, describing an indicator in an epoxy coating detecting steel corrosion.

A desired fluorescent probe for steel corrosion detection should form a complex with ferrous and/or ferric ions (produced at the anodic site during steel corrosion), resulting in “turn-on” fluorescence, in contrast to quenching reactions that are more common with fluorescence probes. This particular “turn-on” reaction of the fluorophore with the metal ion is known as chelation-enhanced fluorescence (CHEF). The initially nonfluorescent indicator, after incorporation into the epoxy coating, would ideally become fluorescent in areas where corrosion occurs before any obvious sign of metal damage can be observed by the naked eye. Also, an ideal fluorescent indicator suitable for epoxy coatings should not change its fluorescence when mixed with precursor components during the preparation of the coating.

Recently, many CHEF probes for complexation with Fe ions have been synthesized for biological applications (13–16). The Fe^{3+} indicator spiro[1*H*-isoindole-1,9'-[9*H*]xanthen]-3(2*H*)-one, 3',6'-bis(diethylamino)-2-[(1-methylethylidene)-amino] (FD1), first synthesized by Zhang et al. (16), was used in this work because of its high selectivity to iron over other metal ions, its relatively easy synthesis, and no expected interaction with epoxy-coating components. The proposed FD1– Fe^{3+} binding mechanism is shown in Figure 1. In the present work, we describe the successful application of FD1 as a smart indicator in epoxy-based coatings for early detection of steel corrosion.

2. EXPERIMENTAL SECTION

2.1. Reagents. Sodium chloride, toluene (ACS grade), chloroform (HPLC grade), ethanol (HPLC grade), acetonitrile (HPLC grade), and acetone (HPLC grade) were purchased from EMD

Chemicals and used as received. Rhodamine B hydrazide was purchased from Fluka Chemical Corp. Acetic acid (glacial, ACS grade) was purchased from VWR Scientific Products. Ferric chloride hexahydrate was purchased from Mallinckrodt. Anhydrous sodium sulfate was purchased from Em Science. Haze Gray Epoxy Polyamide coating, MIL-DTL-24441C, type III, Formula 151, was purchased from NCS Coatings, Inc.

2.2. Apparatus. Fluorescence imaging was conducted on a Zeiss LSM 510 Meta laser scanning confocal microscope with an Axio Imager M1 platform. In all experiments, a 514 nm ArMultiLine laser was used as the excitation source. An EC Plan-Neofluar 10×/0.30 M27 objective was used to observe the sample surface. The fluorescent emission wavelength was obtained from the λ mode function (using a Meta detector with a selected emitted fluorescence range of 520–660 nm with a 10.7 nm step). To compare the laser-excited images to those obtained by more practical end-use conditions, the confocal microscope's 100 W mercury lamp was used as a UV light source. Observation and imaging of the coating sample surface was also performed using an Olympus BH2 optical microscope with a 10× objective and an attached digital SLR camera. Fluorescence emission spectra were obtained with a Cary Eclipse fluorescence spectrofluorometer. The coating thickness was measured with a CHECK-LINE coating thickness tester (model DAC-1KS).

2.3. Synthesis of FD1. The FD1 sensor molecule was synthesized according to a literature procedure (17). Rhodamine B hydrazide (0.688 g) was dissolved in 85 mL of acetone. A trace amount of acetic acid was added as a catalyst, and the whole mixture was refluxed for 5 h. After solvent removal under reduced pressure, the residue was redissolved in chloroform. The chloroform solution was washed with deionized (DI) water and dried over anhydrous sodium sulfate. After chloroform was removed under reduced pressure, the obtained residue was recrystallized from ethanol to give an almost colorless powder. Yield: 0.295 g (43%). The ^1H NMR of FD1 matched that reported earlier (16).

2.4. Preparation of Free-Standing Fe^{3+} -Sensing Epoxy Films. A free-standing Fe^{3+} -sensing epoxy film (free from any substrate) was prepared in order to test the efficacy of the indicator within the epoxy matrix. A commercially available filled epoxy coating system was used to test the fluorescent response in the presence of filler pigments. The coating was prepared by mixing both the amine and epoxide components of MIL-DTL-24441C, Haze Gray Epoxy Polyamide coating, with 1.5 wt % FD1 (based on a dry coating). To aid in uniform mixing with the epoxy components, FD1 was first dissolved in toluene. After mixing, the resin solution was poured into a rectangular-shaped silicone mold and cured at room temperature for 1 week. After curing, the film specimen was cut into a 5.5 cm × 1 cm × 0.05 cm piece and placed in a vial with a 0.002 M FeCl_3 aqueous solution, so that half of the specimen was immersed in the solution. The fluorescent response of FD1 in the free-standing epoxy matrix to Fe^{3+} ions from the solution was observed with the confocal microscope with the excitation wavelength of 514 nm.

2.5. Preparation of Steel Coupons Coated with Fe^{3+} -Sensing Epoxy Films. Corrosion-sensing panels were prepared by applying the Fe^{3+} -sensing epoxy coating (described in section 2.4) onto one side of carbon steel coupons (ANSI 1018 grade; edge ground and sand blasted) with dimensions of 5.3 cm × 7.3 cm × 0.3 cm. Before coating application, the steel surface was washed with acetone. The epoxy coating was applied using a brush applicator. The back of the specimen and its edges were painted with MIL-DTL-24441C, Haze Gray Epoxy Polyamide coating (thinned with toluene), without FD1. The panels were cured at room temperature for 1 week. The coating thickness was approximately 40 μm .

To observe the response of FD1 in the coating to steel corrosion, the coated steel panels were scribed using a razor (scribe length 1.3 mm) and placed horizontally on top of a beaker containing a 0.5 M NaCl solution, exposing their scribed surface to the water vapor. After 40 h, the sample was subsequently placed in DI water for 22 h and was then submerged in a 0.5 M NaCl solution for 30 min to speed up the corrosion process. The area on the coating surface surrounding the scribe was monitored with time for changes in the fluorescence intensity with the confocal microscope. Also pictures of the sample surface under UV light were taken using a digital camera placed on the microscope eyepiece.

2.6. Preparation of Undercoating Corrosion-Sensing Panels. Special panels were also prepared to simulate delamination to test the efficacy of the FD1-containing epoxy coating for sensing of undercoating steel corrosion. The coatings on the steel coupons were prepared by mixing MIL-DTL-24441C, Haze Gray Epoxy Polyamide coating, with 0.5 wt % FD1 (based on a dry coating). Prior to mixing with the epoxy components, FD1 was first dissolved in toluene. Before application of the coatings in this case, the steel coupons (ANSI 1018 grade; edge ground and sand blasted, with dimensions 5.3 cm × 7.3 cm × 0.3 cm) were treated with 10% phosphoric acid to remove any possible corrosion products, washed a few times with acetone, and then dried with compressed air. To mimic a coating defect, a small drop of silicone oil was applied to the steel surface (to deteriorate coating adhesion to the metal surface and to induce a weak point that is susceptible to undercoating corrosion). The filled epoxy coating containing FD1 was then applied to the steel coupon using an air brush applicator. The panel was cured at room temperature for 1 week. The coating thickness was approximately 30 μm.

To initiate the undercoating corrosion, an open-ended glass cylinder was affixed and sealed to the part of the coated panel containing defects. The cylinder was filled with a 5% NaCl solution so that only this circular portion of the sample was exposed to the corrosive environment. The surface of the defect area was monitored with the confocal microscope at different times and temperatures of exposure to the NaCl solution for changes in the fluorescence intensity. Also, pictures of the sample surface under UV light were taken using a digital camera placed on the microscope eyepiece.

3. RESULTS AND DISCUSSION

3.1. Fluorescent Emission Response of FD1 in a Free-Standing Fe³⁺-Sensing Epoxy Film. The fluorescent response of FD1 (1.5 wt % based on a dry coating) embedded in a free-standing epoxy film to Fe³⁺ from a 0.002 M FeCl₃ aqueous solution was monitored by confocal microscopy. Initially, no fluorescence emission of the epoxy film was observed when excited with a 514 nm ArMultiLine laser. After the sample film was immersed in a 0.002 M FeCl₃ aqueous solution for 24 h, a significant increase in fluorescence emission was observed. From the confocal microscope's λ mode function, it can be seen that the maximum fluorescence emission was at 575 nm (Figure 2a), which shifted slightly from the maximum fluorescence wavelength at 583 nm when FD1 was titrated by FeCl₃ in a CH₃CN solution (Figure 2b). A similar shift in fluorescent emission was also reported in other systems when the fluorescent compound was in solution versus in a solid state (18). It can thus be concluded that FD1 in the free-standing epoxy film can chelate with Fe³⁺ from the solution, forming a fluorescent complex.

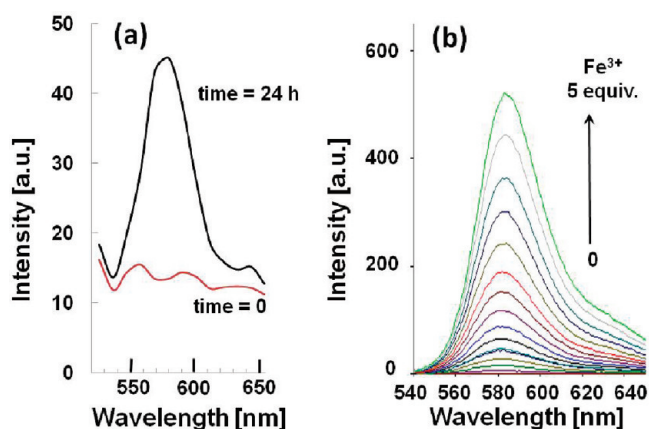


FIGURE 2. Change in the fluorescence emission intensity of (a) a free-standing Fe³⁺-sensing epoxy film with FD1 in a 0.002 M FeCl₃ aqueous solution ($\lambda_{\text{ex}} = 514$ nm) at time 0 and after 24 h (data were transformed from the λ mode) and (b) FD1 in a CH₃CN solution (20 μM) upon the addition of a FeCl₃ solution in CH₃CN (0–5 equiv) ($\lambda_{\text{ex}} = 510$ nm).

3.2. Fluorescent Emission Response of FD1 in a Fe³⁺-Sensing Epoxy Coating on Steel Coupons.

Figure 3 shows the fluorescence images of the scribed area on the Fe³⁺-sensing epoxy coating (1.5 wt % FD1 based on a dry coating) on a steel coupon. The images on the top row of Figure 3 were taken by the confocal microscope when the sample was excited by a 514 nm laser, which is essentially the maximum excitation wavelength for FD1 complexed with Fe³⁺ (510 nm). The confocal microscope images allow quantification of the response by λ-mode analysis (e.g., maximum emission wavelength). The corresponding UV images in the bottom row were taken through the microscope's eyepiece by a digital camera when the sample was excited by a mercury lamp (UV light source). The broader range of excitation wavelengths from the UV source does not excite FD1 at its maximum, yet the fluorescence emission is still visible by eye (at a lower intensity) while one can also simultaneously see the actual coating defects (e.g., the scribe, rust, etc.). The images were recorded at different times of exposure to a corrosive environment. The coated coupon was first placed horizontally on a beaker containing a 0.5 M NaCl solution (sample not immersed in the solution) to observe slow corrosion of the scribed area due to water vapor. Initially, no significant fluorescence was observed by the confocal microscope (Figure 3a, top row). Similarly, under UV light, the area around the scribe looked no different from the rest of the sample (Figure 3a, bottom row). After 40 h, bright areas appeared around the scribe (Figure 3b, top row). From the λ mode (inset in Figure 3b), it can be seen that the maximum fluorescence intensity of these bright areas was at 570 nm (consistent with the maximum shown in Figure 2a), which was due to the formation of the Fe–FD1 complex and indicated that early corrosion had occurred. In our system here, the maximum fluorescence intensity appeared at a wavelength between 570 and 585 nm. To speed up the corrosion process, the coated coupon was then half-immersed in a beaker with DI water (images c and d in Figure 3). Finally, Figure 3e shows the sample after 30 min of immersion in the original 0.5 M

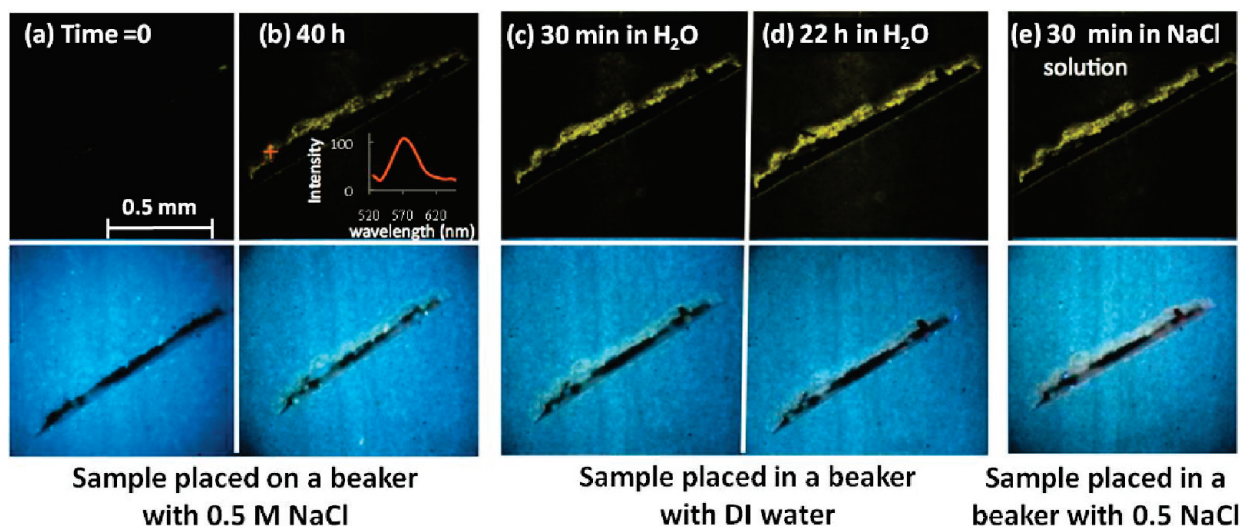


FIGURE 3. Scribed area on the coated steel coupon after various times of exposure to different corrosive environments: a sample placed on top of a beaker with a 0.5 M NaCl solution (a) at time 0 and (b) after 40 h, a sample placed in a beaker with DI water after (c) 30 min and (d) 22 h, and (e) a sample placed in a 0.5 M NaCl solution after 30 min. Top row: fluorescent images taken on the confocal microscope. Bottom row: digital camera images of the same area taken through the microscope eyepiece under UV light. The inset in part b shows fluorescent emission of the point marked by an orange cross on the area around the scribe fluorescing at a maximum intensity of 570 nm; data were transformed from the λ mode.

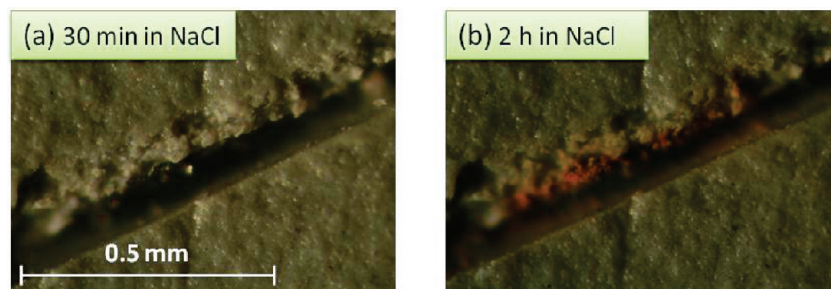


FIGURE 4. Optical images of the scribed area of the corrosion-sensing panel after (a) 30 min and (b) 2 h of immersion in 0.5 M NaCl.

NaCl solution. The FD1 indicator reports the onset of corrosion by the bright-yellow area in the fluorescence images and the yellow-orange areas in the UV images (Figure 3b–e). When compared, however, to the 30 min optical microscope image (Figure 4a), in which the onset of corrosion was not discernible at all to the naked eye, it is clearly evident in the FD1 fluorescent response in Figure 3e. After 2 h of immersion in a NaCl solution, corrosion was finally visible to the eye (Figure 4b). This is very promising data, indicating that FD1 is indeed functioning as an early detection indicator for corrosion. This is crucial in terms of timely maintenance of the metal substrate before too much damage occurs. We are further encouraged by this result considering that the epoxy coating containing FD1 is highly pigmented, which potentially could have reduced the observable fluorescent response from FD1.

It is worth mentioning that our preliminary experiments have shown that FD1 does not leach out of the coating matrix when the coating was immersed in a NaCl solution for 1 month, which is crucial for the long-term applicability of this reporting mechanism.

3.3. Undercoating Corrosion Sensing. In order to mimic an undercoating defect, a small drop of silicone oil was applied onto the steel surface (to deteriorate coating adhesion to the metal surface and to induce a weak point

that is susceptible to undercoating corrosion) prior to coating with the filled epoxy containing FD1 (0.5 wt % based on a dry coating). The application of the silicone oil drop caused visible craterlike defects to appear in the coating surface immediately after coating application. The defective areas are the weak points in the coating. Undercoating corrosion can initiate from these weak spots and develop into blisters (as a result of osmotic action and coating delamination). Blistering is usually the first visual indication of coating failure (19).

Initially, two areas were marked on the panel surface shown in Figure 5a: AREA1 (where silicone oil was initially applied; the area exposed to a NaCl solution is indicated by the blue circle) and AREA2 (where no defects were observed; the area not exposed to NaCl). After the coating was cured and before the panel was exposed to the corrosive environment, no initial fluorescent emission was observed in the coating as viewed under the confocal microscope in both of the marked areas (excitation wavelength $\lambda_{\text{ex}} = 514$ nm). After 1 day of exposure to a 5% NaCl solution, a craterlike blister appeared (3 mm diameter) in one of the defective areas, indicated by the red circle in Figure 5a. Nonetheless, the coating remained intact, and there was no visible sign of any corrosion. When the fluorescence measurement was performed on this panel using the confocal microscope, a

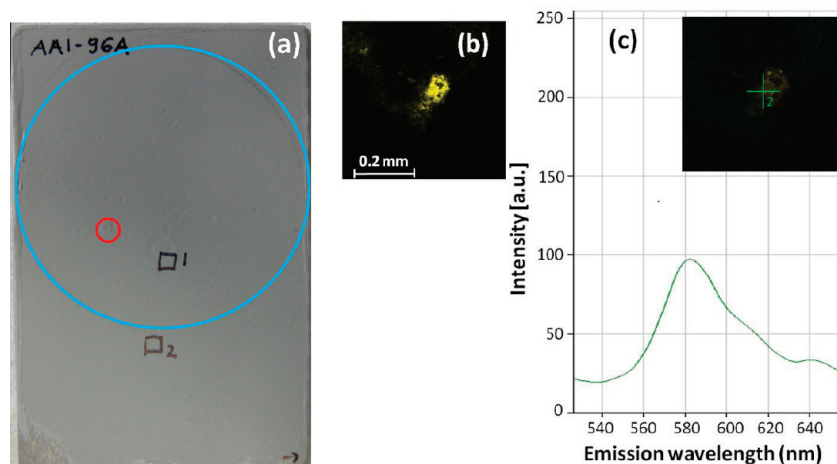


FIGURE 5. (a) Undercoating corrosion-sensing panel after 1 day of exposure to a 5% NaCl solution. Blue and red circles represent areas exposed to NaCl and a blister, respectively. "1" and "2" represent the area exposed to a NaCl solution where silicone oil was applied and the area that was not exposed to the NaCl solution, respectively. (b) Fluorescence image of the area in the red circle taken on the confocal microscope and (c) the λ mode of the same area.

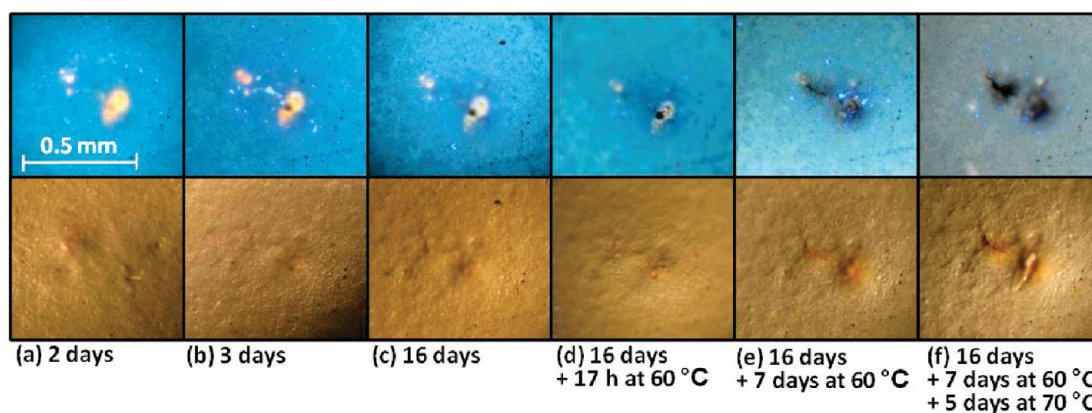


FIGURE 6. Images of a blister in an undercoating corrosion-sensing panel after immersion in a 5% NaCl solution under different conditions. Top row: images taken under UV light. Bottom row: images taken under natural light.

bright spot in the middle of the blister (Figure 5b) was observed. From the λ -mode function, we observed that the maximum fluorescence intensity in this spot was at 580 nm (Figure 5c), as expected. Also, under UV light, the same spot appeared to be yellow-orange. These observations clearly pointed to the *undercoating* corrosion that had occurred after 1 day of immersion in a NaCl solution.

After 2 days of exposure to a 5% NaCl solution, other bright areas appeared within the blister (Figure 6a, top row). It is important to note that in the same area, under the microscope in natural light, we did not observe any visible sign of corrosion (Figure 6a, bottom row). After 3 days, small dark spots started to appear in the bright area (Figure 6b, top row) under UV light. In natural light, the same dark spot had a rusty color (Figure 6b, bottom row). After 16 days of exposure, both the dark spot (in UV light) and the rusty area (in natural light) slightly increased in size (Figure 6c). Also from λ mode, we observed a corresponding decrease in the fluorescence intensity in those areas, likely because of deposition of the corrosion products (rust). To facilitate the diffusion of the corrosive solution to the metal/coating interface, the coated panel was then placed in an oven at 60 °C. After 17 h at 60 °C (and in a 5% NaCl solution), more dark precipitation was observed in the previously bright area

(Figure 6d, top row). At the same time under natural light, the rusty spot was easily observable in the same area (Figure 6d, bottom row). After 7 more days in the NaCl solution at 60 °C, the rusty areas were significantly larger and could be easily seen under both UV and natural light (Figure 6e). The coated panel was then subsequently placed at a higher temperature (70 °C) for another 5 days. After that time, we observed a further increase in the size of the rusty areas in the blister under the microscope (Figure 6f, bottom row). By this time, the rusty spot could also be seen by the naked eye without a microscope. Also, throughout the blister, some bright-yellow-orange spots (under UV light) appeared. The maximum fluorescence intensity of these bright spots was the same as that in the initial bright areas in the blister. Those areas are potentially new onsets of corrosion. It should also be noted that the whole area investigated under the UV light (which is the same in size as the blister area) changed color intensity from bright blue to a more faded greenish-blue over time during the testing. This color change might be explained by prolonged exposure to high-power UV light during the imaging. Over the course of this experiment, no fluorescence was observed in AREA2, as expected, confirming that corrosion only occurred in areas in contact with a NaCl solution.

We are currently investigating the lower limit of the FD1 concentration in the epoxy coating for adequate fluorescent response, persistence of the fluorescent response after the onset of corrosion, and the stability of FD1 in a coating on a noncorroding substrate over time.

4. CONCLUSIONS

We have demonstrated that FD1 is very effective for indicating early corrosion of steel covered with an epoxy coating, for both areas damaged through to the substrate (scribed areas) and areas without exposure of the substrate (*undercoating* corrosion). The “turn-on” fluorescence via chelation between FD1 and ferric ions can be captured not only by a confocal fluorescent microscope but also by, more conveniently, an optical microscope with UV light, which allows us to easily and nondestructively detect early corrosion of steel before any visible sign of corrosion appears. In addition, only a low FD1 concentration (0.5 wt %) in the coating is needed. FD1 does not prematurely interact with coating formulation components, and FD1 can “report” early corrosion even in the presence of pigments.

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