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UMI
DEVELOPMENT AND CHARACTERIZATION OF CORROSION SENSING COATING SYSTEMS

DISSERTATION

Presented in Partial Fulfillment of the Requirements for the
Degree Doctor of Philosophy in the Graduate School of
The Ohio State University

By
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1999

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The early detection of corrosion in aging aircraft has both economic and safety implications. In this thesis, new corrosion sensing coating systems based on acrylic, epoxy-polyamide, and agar-gel modified by pH indicators or fluorescence compounds are developed. The pH increase from cathodic reactions associated with corrosion is expected to be effectively monitored by this approach.

The corrosion detection sensitivity of acrylic-based coating systems was determined by applying constant cathodic current and measuring the charge at which color change or fluorescence was detected. Visual observation of coated samples with the unaided eye can detect changes resulting from a charge corresponding to a hemispherical pit with depth on the order of 10 μm. The pH sensing characteristics of modified acrylic coating systems were studied by titration tests.
The corrosion sensing coatings developed were characterized by Fourier Transfer Infrared Spectroscopy (FTIR) and Electrochemical Impedance Spectroscopy (EIS). EIS results showed that the indicating compound addition had little effect on the coating corrosion protectiveness. EIS also demonstrated that the time for color change was determined by the sensitivity of the coating to pH changes, and not by the coating protectiveness. FTIR results suggested that no structural changes occurred in the acrylic paint before and after modification by phenolphthalein, bromothylmol blue, and 7-hydroxycoumarin. The conclusion can be made that the addition of indicators or fluorescing compound did not produce significant structural changes. The mixture of indicator and polymer apparently resulted only in physical blending.

Another corrosion detection method, which uses modified agar-gel as a corrosion-sensing medium, is also introduced in this thesis. This coating could be applied and quickly removed after noting the location of corrosion. Color change or fluorescing compounds that are sensitive to pH were added to the agar gel in order to sense the pH change associated with the cathodic reaction that accompanies corrosion. The formation and structure of the modified agar-gel are discussed. Corrosion sensing behavior associated with the time for initial color change or fluorescing was demonstrated to be dependent on gel composition, corrosion initiation conditions, and surface conditions before applying the gel coating.

Several selected pH indicators or fluorescing compounds were also incorporated into epoxy polyamide (EP) paint, which is a standard primer for aerospace applications. The corrosion sensing behavior has been determined and the results were explained by the pH sensing properties of modified epoxy paint from titration experiments. The results
showed that color change pH indicators could be used to modify the epoxy coating to
sense the cathodic reaction as long as the overall pH value was adjusted to below the
critical pH value of color change for pH indicators. The fluorescing interference from
both the resin and hardener components made it difficult to use fluorescence compounds
for corrosion detection. Corrosion sensing properties of modified EP coating after
dilution have been shown to depend on the pH sensing behavior of modified coating
systems. Indicator-containing epoxy coatings formed with neutralization and dilution
appear to be promising candidates as effective corrosion sensing primer coatings
TO MY WIFE, YAN MA
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Any effective corrosion detection scheme must be based on a fundamental understanding of the corrosion process in the coated metal structure. In this chapter, three major types of corrosion under polymer coatings are reviewed: blisters, filiform corrosion, and cathodic delamination. The mechanisms are discussed in terms of different coating systems and environmental effects. Electrochemical impedance spectroscopy (EIS) techniques for coating evaluation are introduced and reviewed, including the traditional equivalent circuit analytical methods and breakpoint frequency for coating defect analysis. Efforts in developing corrosion sensors are also discussed in this chapter. The corrosion sensing coating approach used in this study is shown to be promising based on the fact that separation between cathode and anode is prevalent during corrosion under coatings.
1.1 BACKGROUND

Corrosion is a very common means by which materials degrade during service, especially metals. According to D.A. Jones, [1] "Corrosion is the destructive result of chemical reaction between a metal or metal alloy and its environment." The economic costs of corrosion in the USA alone have been estimated to be 4.2% of the GNP per year [2]. According to its different appearances and driving forces, corrosion can be divided into uniform corrosion, galvanic corrosion, crevice corrosion, pitting corrosion, environmentally induced cracking, hydrogen damage, intergranular corrosion, dealloying and erosion corrosion [1]. The three major methods for corrosion control are cathodic protection, the use of materials with high intrinsic corrosion resistance, and the use of corrosion protective coatings. Organic coatings are widely used to combat corrosion due to their low cost and high degree of effectiveness. For organic coated structures (e.g. airplanes), the coating properties and corrosion underneath the coating are of major concern. A better understanding of under coating corrosion processes would be helpful for coating development and, especially, for development of effective corrosion detection methods.

The detection of localized corrosion in a large complex structure such as an airplane is critical, but practically very difficult. For a painted structure, it is possible for the organic coating itself to serve as a corrosion sensor since it covers the entire surface. Understanding the corrosion behavior of the underlying substrate and the subsequent changes in the coating system is the key in developing this non-destructive sensing approach. In this chapter, the three predominant mechanisms of corrosion under coatings
are described: blisters, filiform corrosion and cathodic delamination. In order to detect these damage processes in their early stage, a vivid corrosion detection scheme has been devised. This technique is based on detecting the pH change associated with the cathodic reaction of the corrosion process occurring at the interface between the metal surface and coating. The key practical issues are (1) making the pH change easily recognizable and (2) quantifying the magnitude of the change. This chapter reviews the damage processes, and describes the development work on this corrosion detection scheme. It is proposed that paint can be used as a corrosion sensor when it has enough sensitivity to detect the initial stage of corrosion damage.

Electrochemical impedance spectroscopy (EIS), one of most important corrosion evaluation techniques for coated metal, will also be reviewed and compared with the newly developed coating sensor techniques.

1.2 CORROSION UNDER ORGANIC COATINGS

Organic coatings comprise the primary method for corrosion protection because of their barrier properties and, in some cases, their ability to provide active corrosion protection. However, due to their semi-permeable characteristics [3-5], it is inevitable that water, oxygen and various electrolyte ions will eventually diffuse through the coating to the metal-coating interface and initiate corrosion at the interface between the metal surface and organic coating. Corrosion failures of organic coated metals can occur by a number of different mechanisms, including blistering, filiform corrosion, cathodic
delamination, early rusting, and anodic undermining. The first three types of coating defects will be discussed in this chapter. Anodic undermining and early rusting are not addressed in this review since they are less detrimental and very little systematic research has been conducted on them.

1.2.1 Blistering

Blistering is one of the first signs of breakdown in a protective coating. The blisters are local regions where water accumulates and corrosion begins. Five mechanisms have been developed to explain blister formation [3,6]. These include blistering due to volume expansion and swelling [4-6], blistering due to gas inclusion or gas formation [3], electroosmotic blistering [7,8], osmotic blistering [6,7,9] and blistering due to phase separation during film formation [10]. In all cases, the blister is a locality where under-film electrolyte has developed through permeation of water and ions from the environment, and leaching of ionic materials from the interface or from the coating. Blistering permits corrosion that consists of metal dissolution supported by the oxygen reduction, equation 1-1.

\[
2\text{H}_2\text{O} + \text{O}_2 + 4e^- = 4\text{OH}^- \quad (1-1)
\]

pH values close to 14 have been measured in liquid underneath a coating on steel near a defect using a pH-sensitive electrode inserted through the substrate [11]. Corrosion products tend to concentrate on the inside dome of the blister and the anodic region is in the center of the blister, where the oxygen concentration is the lowest. The
periphery in the blister is cathodic since the oxygen availability is greater there [12]. Among all the mechanisms mentioned above, the osmotic pressure gradient, which results from the water activity difference between the two sides of the coating, is the principal mechanism responsible for blister formation [13,14]. A physical model has been developed by Nguyen et al. [15] that describes blistering resulting from the corrosion of coated metals containing defects. This model is based on the diffusion of cations through some arbitrary medium, Figure 1.1. The physical background of the model is that cations migrating along the coating/metal interface from the defect to the cathodic sites are assumed to be responsible for the formation of concentrated localized electrolyte, for example NaOH. High water solubility of this salt causes a difference in the thermodynamic activities of water between the exposure environment and the coating/metal interface, which drives osmosis and leads to blistering [8]. Cation diffusion plays an important role in the blistering process and different cation diffusivities lead to different blistering rates. It was demonstrated [8] that the rate of blistering of zinc chromate containing alkyd on steel under comparable conditions decreased in 1.0 M solutions in the order: KCl>NaCl>LiCl, Figure 1.2. This behavior was explained [8] on the basis of the transference numbers of the alkali metal ions and the diffusion coefficients of the cations in the coating. Others [10] studied the effect of coating solvents on the mechanism of blister formation and concluded that the solubility of water in the tail solvent of a filament can be inversely correlated to the resistance of the applied paint.
1.2.2 Cathodic Delamination

Cathodic delamination often occurs near coating defects after coated metal exposure to the corrosive environments. There are many defects that can initiate delamination. These include scratches, abrasions, cracks in the organic coating caused by forming operations, tiny gaps, and capillary paths in the coating film or a corrosion process under film. The existence of such areas will induce a galvanic cell in which the organic coated metal is the cathode, Figure 1.3 [16]. Several mechanisms have been developed to account for this kind of coating failure. The first is that coatings are highly susceptible to disbondment as a result of reaction of the film with the cathodically produced alkali at the interface [16,17]. The second is based on the ability of an alkaline solution to creep over the surface to displace the organic coating from the metal surface [18]. The third is the reduction of the metal oxide to which the organic coating is attached [16,19,20].
Figure 1.1. Cathodic blistering and delamination of a scribed coated steel panel exposed to NaCl solution [15].
Figure 1.2. Percentage of area blistered as a function of time for a 2.5 μm thick zinc chromate alkyd coating at 60°C and an applied potential of –900 mV (vs SCE) [8].
It is difficult to cathodically detach organic coatings from aluminum and chromium-chromium oxide coated steel by this mechanism because their oxides are not easily reduced [20]. The rate of delamination depends on variables that affect the flow of constituents to the reactive site where the delamination is occurring and the rate of reaction at the site of disbondment [20]. The paths by which reactants can reach the delaminating front are through the coating, and across the metal-coating interface from a defect. Diffusion of species through the coating is supported as the rate limiting step by the fact that the rate of delamination decreases with increase in film thickness [21]. Evidence supporting lateral diffusion of species as the rate-limiting step comes from the experiments carried out in a two-compartment cell. The delamination begins in one cell where the coating plus defect is in contact with one corrosive medium, and continues beneath an “O” ring into a second compartment in which the coating is in contact with a second less corrosive medium [16].

1.2.3 Filiform Corrosion

**General characteristics**

The phenomenon of filiform corrosion has been known for about 70 years. The term "filiform" corrosion was first used by Sharman [22] to describe the growth of hair-like corrosion tracks – a kind of underfilm corrosion. Actually, filiform corrosion is a moving corrosion cell underneath a surface film (coating or oxide film) leaving an inert tail filled with corrosion products. An example of filiform corrosion under a coating on aluminum aircraft skin is shown in Figure 1.4 [23].
Figure 1.3. Model for the cathodic disbonding process [16].
Filiform corrosion has been found under different kinds of coatings. Filamentary corrosion tracks were observed by Van Loo et al. [24] under several kinds of paints on iron and under a variety of metal coatings, for example tinplate, silverplate, and goldplate. Hargreaves [25] has observed filiform corrosion on nickel-plated iron. Filiform corrosion was also observed on steel, aluminum alloys, and magnesium alloys.

Three types of filiform attack have been described in the literature. The first is filamentary corrosion beginning at a defect in the coating where the metal substrate is exposed to a corrosive environment [22,26]. The second is filamentary corrosion on metal such as aluminum alloy [26] or steel [25,27] covered with a thick oxide film. The last is a type of underfilm corrosion caused by a chain of interconnected blisters that periodically rupture, resulting in filimentary tracks that resemble worm-like filiform corrosion [25,27,28]. Steele [26] and Ruggeri [29] proposed the following common features of filiform attack: (a) filiform corrosion initiates at a break, or defect in the surface coating and the basic motion proceeds linearly, although the direction can be arbitrary; (b) the filaments produced as a consequence of corrosion are generally between 0.1 and 0.5mm wide and typically grow at speeds around 0.15 – 0.4 mm/day; (c) tracks do not cross one another, or breaks in the surface coating; (d) the front edge of the head contains a solution of low pH and appears to be the most anodically active area; (e) water is required, but filiform occurs only within a limited range of relative humidity (filiform corrosion will not occur if RH>95%); (f) oxygen is required for filiform corrosion to propagate, (no corrosion will occur under a helium or nitrogen atmosphere).
Figure 1.4. A typical filiform corrosion under coating on aluminum aircraft skin [23].
and (g) the size and speed of filaments are insensitive to the physical properties of the coating.

This review focuses on the first type of filiform corrosion that originates at a defect in the coating on the metal substrate where some soluble ionic species are present. The so-produced filamentary track is composed of two parts: the head and the tail. Corrosion takes place in the head filled with a liquid solution and the tail is filled with corrosion products that are inactive, Figure 1.5.

**Mechanisms**

Many studies on the mechanism of filiform corrosion have been made since Sharman presented his work in 1944 [22]. It is generally accepted that the driving force for filiform corrosion is a type of differential aeration cell in which the separated anodic and cathodic areas correspond to deraerated and aerated areas [16,26,29,30]. Potential and pH measurements indicate that the front of the head is the most anodic site, and the primary cathodic site is at the back of the head. Slabaugh et al. [31] measured the potential at the tip of the filamentary head to be about \(-0.96\) V (SCE), with a potential difference in solution between the front and the back of the head of about \(0.09\) V. This polarity is such that cations migrate toward the back of the filamentary head. Others [30] have measured a potential difference of \(0.02\) V between the anodic and cathodic area using a simulated cell. In this case, the corrosion current density was determined to be \(60\) mA/cm\(^2\) when the cathodic to anodic area ratio was 100:1 for aluminum. The pH variation at the sites of head (front, back) and tail of filamentary tracks was observed by several authors, as shown in Table 1.1.
Figure 1.5. The present model of filiform corrosion showing the primary reaction zones (head and tail) and mass transfer within the filiform head [26, 29].
<table>
<thead>
<tr>
<th>Location</th>
<th>pH value</th>
<th>Coating</th>
<th>Metal</th>
<th>RH(%)</th>
<th>T(°C)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Head</td>
<td>1.0</td>
<td>Polyurethane</td>
<td>Al</td>
<td>75</td>
<td>RT</td>
<td>Hoch, 1971[30]</td>
</tr>
<tr>
<td></td>
<td>1.5 - 2</td>
<td>Various</td>
<td>Al</td>
<td>85</td>
<td>40</td>
<td>Slabaugh, 1972 [31]</td>
</tr>
<tr>
<td>Acid (pH paper)</td>
<td>Various</td>
<td>Mg</td>
<td>75</td>
<td>25</td>
<td>Holler 1963[32]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>12 (at the rear)</td>
<td>Urea-alkyd</td>
<td>Cold rolled steel</td>
<td>85</td>
<td>RT</td>
<td>Slabaugh and Grotheer, 1954[32]</td>
</tr>
<tr>
<td>Tail</td>
<td>3.5-alkaline</td>
<td>Polyurethane</td>
<td>Al</td>
<td>75</td>
<td>RT</td>
<td>Hoch, 1971[30]</td>
</tr>
<tr>
<td></td>
<td>&gt; 10</td>
<td>Various</td>
<td>Mg</td>
<td></td>
<td></td>
<td>Hoch, 1971[30]</td>
</tr>
</tbody>
</table>

Table 1.1 Summary of Measured pH Value and Other Related Condition on Filiform Corrosion
According to the Pourbaix diagram, ferric hydroxide and aluminum hydroxide must be accumulated in the tail for iron and aluminum, respectively. The ferric hydroxide eventually dehydrates to form ferric oxide. Within the head, ferrous hydroxide or Al(OH)$_3$ gel forms due to hydrolysis reaction and the cations migrate to the back of the head under the potential gradient [30,31]. Under the same potential gradient, chloride anions migrate toward the front of the head. The key point for forming and sustaining this electrochemical reaction cell within the filiform head is the mechanism of water and oxygen transport to the head. A variety of mechanisms have been proposed. Some authors [16,30] have suggested that paint coatings must be semipermeable membranes and that filiform corrosion is controlled by diffusion of water and oxygen through the paint. However, other results [29,31,33] show that filiform corrosion is relatively insensitive to the type of the coating covering the substrate metal. On the basis of these results, Kaesche [34] proposed that the porous tail may serve as a pathway for transport of water and oxygen. This transport mechanism has been further developed by Ruggeri [29] and Steele [26] in their quantitative analysis of the mass transport during the filiform corrosion process, Figure 1.5. The rate of diffusion was calculated to be about ten times that required to support corrosion and more than ten times the maximum value for diffusion through a polymer coating. Furthermore, the asymmetry and directionality of filiform corrosion preclude the possibility of diffusion through the coatings [26,29].
1.3 REVIEW OF EIS TECHNIQUES FOR COATING EXAMINATION

1.3.1 Background

The advantage of EIS over DC measurement

Electrochemical impedance spectroscopy (EIS) has become a very important technique for analysis of many electrochemical processes, such as batteries, electro-deposition, and corrosion, that involve sub-processes such as electrochemical reactions, chemical reactions, adsorption, and diffusion. The presence of an organic coating introduces additional electrochemical and electrical properties (e.g. coating capacitance and resistance), which cannot be distinguished by simple DC measurements. AC techniques have a number of advantages over traditional DC techniques [35-39]. First of all, by using AC excitation, only those processes that have sufficient time to occur during the alternation of the electric field are observed. Each process can be described by applying an input signal over a range of frequencies and the modeled parameters for these electrochemical interfaces can be derived by curve fitting through a suitable electric circuit. Secondly, it is possible, by using this technique, to study corrosion reactions in low conductivity media where DC measurements are impossible if the ohmic drop is not eliminated [39]. Finally, EIS can be performed while the system is under steady state conditions using a small-amplitude perturbation, thus eliminating polarization induced damaging effects.
**Important concepts**

(a) **Impedance**

Impedance \((Z)\) represents the ac equivalent of resistance. According to Ohm’s law, the impedance of the electrochemical system can be calculated as equation 1-2:

\[
Z = \frac{E(t)}{I(t)} = \frac{E_0 \cos(\omega t)}{I_0 \cos(\omega t - \phi)} = Z_0 \frac{\cos(\omega t)}{\cos(\omega t - \phi)}
\]  

(1-2)

where \(t\) is the time, \(\omega\) is the radial frequency, \(E_0\) and \(I_0\) are the amplitude of the input (potential) and output (current) signal, \(Z_0\) is the magnitude of the impedance and \(\phi\) is a phase shift between the potential input and current response. The above impedance can also be represented as a complex number: \(Z = Z_0 (\cos\phi + jsin\phi) = Z' + jZ''\), where \(Z'\) and \(Z''\) represent the real and imaginary parts of impedance.

(b) **Equivalent circuit and data presentation for EIS test of coated sample**

A corroding system can be described in terms of an equivalent circuit, whose various elements pass current with the same amplitude and phase angle as does the corroding system under a given excitation. There are many different equivalent electric circuits that have been developed to model the corrosion processes for coated metals. The most popular one, shown in Figure 1.6, has been proposed by many authors in different forms [40-43]. Besides the elements shown, a Warburg or diffusion impedance is sometimes used in series with \(R_{ct}\) to represent the diffusion control corrosion process at the metal-polymer coating interface.
Figure 1.6. Electrical equivalent circuit models describing coated metal systems: (a) Defect-free coating and (b) Organic coating containing defects. (Rs is charge transfer resistance associated with corrosion at exposed metal sites, Rs, Rp and Rt refer to the resistance of solution, pore in the coating and charge transfer, Cc and Cdl are the coating and double layer capacitors, CPE is constant phase element associated with non-ideal capacitance).
In addition, an inductor (L) is sometimes used in the circuit, which is thought to result from an adsorption effect or inhomogeneous current distribution. Constant phase elements (CPE) are also applied when systems do not behave as ideal capacitors. In general, all the elements used in the equivalent circuits are presented in Table 1.2, in which equations for both the admittance and impedance are given for each element.

Nyquist and Bode plots are two widely used data presentation methods in EIS. Typical plots for a polymer coated metal substrate are given in Figure 1.7. The important parameters such as $R_s$, $R_{po}$, $R_t$, $C_c$ and $C_{dl}$ can be easily read and key processes associated with interface reactions can be delineated from these plots, as will be discussed in a later section.
<table>
<thead>
<tr>
<th>Equivalent element</th>
<th>Admittance</th>
<th>Impedance</th>
</tr>
</thead>
<tbody>
<tr>
<td>R</td>
<td>1/R</td>
<td>R</td>
</tr>
<tr>
<td>C</td>
<td>jωC</td>
<td>1/ jωC</td>
</tr>
<tr>
<td>L</td>
<td>1/ jωL</td>
<td>jωL</td>
</tr>
<tr>
<td>W (infinite Warburg)</td>
<td>1/(σω⁻¹/²(1-j))</td>
<td>σω⁻¹/²(1-j)</td>
</tr>
<tr>
<td>Q (CPE)</td>
<td>Y₀( jω)α</td>
<td>1 / Y₀( jω)α</td>
</tr>
</tbody>
</table>

**Table 1.2.** Circuit Elements Used in the Electrical Equivalent Circuit Models
Figure 1.7. Nyquist and Bode plots calculated for a polymer coated metal substrate which has developed an electrolytic path to the polymer/metal interface, the relaxation for $R_{\text{pore}}C_C$, $R_tC_{\text{dl}}$ and the Warburg impedance $W$ are shown [51].
1.3.2 Application of EIS in Coating Systems

EIS has been successfully applied in many aspects of corrosion behavior such as general corrosion [44,45], localized corrosion (pitting) [44-47], stress corrosion cracking [48], corrosion in low conductivity media [39], and corrosion under coating systems [49-51]. The most successful application of EIS has been in the evaluation of the corrosion behavior of polymer coated metals [37,38]. EIS results have been found to correlate well with results from salt spray tests and have been used as a fast way to conduct lifetime prediction for coatings [52]. For coated samples, in general, EIS provides a measurement of the resistance of the film to transport of ions and water. The equivalent circuit model for organic coatings shown above (Figure 1.6) is generally accepted. However, interpretation of the meaning of the elements and the test approach for applying EIS data for coating evaluation is still controversial. Two aspects of EIS application for coating evaluation, namely determination of barrier behavior of coating systems and coating disbonding evaluation, have attracted a lot of attention. They will be discussed in detail presently.

**Barrier behavior of coating systems**

The barrier properties of corrosion protective organic coatings are of extreme importance. Brasher et al. [32] studied paint films and noted that capacitance and resistance values changed abruptly when the protective nature of the paint deteriorated. It was proposed that the coating capacity, $C_c$, and pore resistance, $R_{po}$, are the two most important parameters for coating property evaluation, and can be used to evaluate the barrier behavior of organic coatings [44,45,53-58].
Coating capacitance \( (C_c) \)

Coating capacitance is related to the exposed area \( A \), coating thickness \( d \) and dielectric constant of the coating \( \varepsilon \):

\[
C_c = \varepsilon \varepsilon_0 A / d \quad (1-3)
\]

where \( \varepsilon_0 \) is the free space electric permittivity and is equal to \( 8.85 \times 10^{-12} \) F/m. Water uptake changes the dielectric constant of the polymer coating and therefore the total capacitance of the coating. The change of \( C_c \) with time has been used extensively to study the water content of coatings on metal surfaces. Brasher's equation (equation 1-4) provides water content, \( \Phi \) (volume fraction of water penetrated), from capacitance values, and has correlated well with gravimetric measurements [32,40]:

\[
\Phi = (\log C_t / C_0) / \log 80 \quad (1-4)
\]

where \( C_t \) is the capacitance at time \( t \), \( C_0 \) is the capacitance at time \( t = 0 \), and 80 is the dielectric constant of water at 25°C. It assumed in this equation that (1) water is homogeneously dispersed, (2) there is no water-polymer chemical interaction and (3) only a small volume of the matrix is penetrated and there is no swelling of the matrix.

The water uptake behavior of coatings can indicate the different periods of coating failure, which consist of three distinct ranges, Figure 1.8. Bonora et al. [51] observed that the typical evolution of \( \Phi \) vs time showed a rapid increase during the first
few days of immersion, which was proposed by Touhsaent and Leidheiser [59] to be the
entry of solution into the defects in the coating, reaching a constant value, $\Phi_s$. $\Phi_s$ can be
correlated with corrosion protection of coating systems. The subsequent increase of $\Phi$
(or capacitance $C$) after a long plateau period is related to detachment of the coating from
the substrate due to the accumulation of water at the metal/coating interface [59,60].

(b) **Pore resistance ($R_{po}$)**

$R_{po}$, the pore resistance of the coating due to electrolyte penetration, has been used
extensively as a measure of coating performance [43,60-62]. The initial application of
DC resistance measurements for monitoring the corrosion of painted metal surfaces was
attributed to Leidheiser [36]. A general quantitative range for the resistance of a good
coating was shown to be $>10^8$ ohm-cm$^2$, and poor coatings were associated with
resistances of $<10^6$ ohm-cm$^2$ [61]. It has been showed that the corrosion resistance of
coatings with four different thicknesses by comparing the $R_{po}$, Figure 1.9. Some of the
coatings contained an artificial defect. Thicker coatings did show some time variation of
the measured resistance.
Figure 1.8. A typical curve of coating capacitance $C_c$ (or water uptake percent $\Phi$) with immersion time, showing the three water uptake domains.
The reason is that a small number of pores developed and then, somehow, became plugged again by the corrosion products. Thin coatings and coatings with artificial defects exhibited a continual decrease in resistance, as might be expected with the development of larger and more pores and an increase in reactive metal surface [61]. The coating rankings based on $R_{po}$ at 11 days were the same as the ASTM D 610 [63] rating method of corrosion area determination. It will be shown below that $R_{po}$ can be related to the area of exposed film that has delaminated from the substrate. The decrease in the average measured coating pore resistance with time reflects an increase in the highly defective areas. Actually, $R_{po}$ has been applied as one of the methods to evaluate the delamination behavior of coated samples by many authors [58,64,65].

The use of EIS for determining the resistance of a coated metal system usually involves measurements in the low-frequency range (i.e., $10^{-2}$ to $10^{-3}$ Hz), which require long measurement times. The validity of experimental data is sometimes questionable due to the unstable surface condition during prolonged immersion times. To deal with this problem, evaluation methods using high-frequency EIS parameters associated with longer relaxation times have been developed by Haruyama et al., as is described in the next section [64,66].
Figure 1.9. \( R_{po} \) as a function of time for the four samples. The thick coating (4.3 \( \mu \)m) showed the time variation of the measured resistance while thin coatings (2.8, 3.2 \( \mu \)m) and coatings with artificial defects exhibited a continual decrease in resistance [63].
Coating disbonding evaluation

The delaminated area \( (A_d) \) under the coating has often been calculated by comparing the measured double-layer capacitance \( (C_{dl}) \) with the specific capacitance value \( (C_{dl}^0) \) (capacitance per unit area) according to the following equation:

\[
A_d = \frac{C_{dl}}{C_{dl}^0}
\]  

(1-5)

\( C_{dl}^0 \) can be either measured on the bare metal exposed to the same electrolyte or considered to be similar to that of mercury, e.g. 15-30 \( \mu F/cm^2 \) [67]. Haruyama et al. [64,66] proposed that all passive elements present in the equivalent circuit, except the coating capacitance \( C_c \), can be applied to calculate the delaminated area, as shown in equations 1-6 - 1-8:

\[
R_{po} = \rho \frac{d}{A_d} = R_{po}^0 / A_d
\]  

(1-6)

\[
R_{ct} = R_{ct}^0 / A_d
\]  

(1-7)

\[
C_{dl} = \varepsilon \varepsilon^0 \frac{A_d}{d} = C_{dl}^0 A_d
\]  

(1-8)

where \( R_{po} \), \( R_{ct} \), and \( C_{dl} \) are pore resistance of the coating, charge transfer resistance and double layer capacitance, respectively. All parameters with the superscript "0" are the area-specific values. The above relationships are based on the assumptions that coating resistivity, \( \rho \), does not change with time, current flow occurs only in the delaminated area \( (A_d) \) and negligible current passes through the intact coating. Others [68] found that \( R_{po} \).
is not an indication of the delaminated area and the coating capacitance (represented by a constant phase element) increases with delamination at longer periods of exposure.

The breakpoint frequency \( f_b \) is the frequency at which the phase angle reaches 45°, Figure 1.10 [58], as the dominating element in the EIS response changes from the coating capacitance to the pore resistance. It was found [62,66] that \( f_b \) increased linearly with defect area and, according to Haruyama, a relationship exists between the disbonded area and \( f_b \):

\[
f_b = 1/(2\pi R_{po}C_c) = f_b^0 A_d / A = f_b^0 D
\]

where \( D = A_d / A \) is the delamination ratio, \( f_b^0 \) is the break point frequency when \( A_d = A \) (total surface area) and was defined by Scully [69] as a characteristic constant of the coating materials:

\[
f_b^0 = (1/2 \pi \rho \varepsilon \varepsilon_0)
\]

where \( \rho \) is the pore electrolyte resistivity and \( \varepsilon \) is the dielectric constant for the fully filled water coating (approaches 80). \( f_b^0 \) depends only on the coating parameters \( \rho \) and \( \varepsilon \) and is independent of coating thickness [66].
Figure 1.10. Bode plot for degraded coated steel showing four breakpoint frequencies, $f_s$, $f_b$, $f_m$, and $f_{lo}$, and phase angle minimum $\Phi_{\text{min}}$ and its frequency $f_{\text{min}}$ [62].
In another study [64], the pore size was also connected with the extended breakpoint frequency, which is another breakpoint (phase shift of 45°) in the low frequency range, and the existence of pores accelerated the rate of delamination of the coating. The above propositions were based on the assumptions of a stable coating dielectric constant, a constant pore electrolyte resistivity, or that the product of these two terms remains constant. The breakpoint frequency has also been applied to predict the long term coating behavior [69]. It was shown by Kendig and Scully that $f_b$ increased well before visual corrosion was detected [70,71]. A log function of $f_b (10 - 2\log f_b)$ was defined as a protection index in comparison with ASTM D 610 rating method [70]. Samples with a value of $(10 - 2\log f_b)$ less than 4 after 10 days of exposure had ASTM D610 ratings below 7 after 550 days of exposure. The second breakpoint frequency $f_{io}$ ($f_{iso}$), Figure 1.10, was studied by Hack and Scully [72] and compared to $f_b (f_{is} \text{ hi})$. $f_{io}$ was related to the second time constant in Figure 1.6 associated with transition from the charge transfer resistance $R_{ct}$, or pore resistance $R_{po}$ (depends on the thickness and degree of intactness of the coating) to the double-layer capacitance $C_{dl}$. It was assumed in their study that exposed metal area was the same as the coating pore area. $f_{io}$ was shown to vary linearly with pore area for small ($10^{-4}$ percent) pore percentages and then become independent of the pore area at $>10^{-3}$ percent porosity. $f_b$ was seen to be linear with pore area in the range of $>0.01$ percent. $f_b$ was detectable but nonlinear in the range of $10^{-4}$ to $10^{-3}$ percent, and undetectable at less than $10^{-4}$ percent, Figure 1.11. Therefore $f_{io}$ was suggested to be a better monitor for early coating breakdown while $f_b$ would be applicable to the later stages of coating breakdown as well as to initially poor coatings.
Due to water uptake of the coating, $\varepsilon$ will increase and $\rho$ will decrease as conductive paths and defects develop in the coating [54,73-75]. Therefore $f_b^0$ is actually not a constant value but is expected to depend on exposure time. In addition to $f_b$, it is also possible to use the minimum of the phase angle, $\phi_{\text{min}}$, and its frequency, $f_{\text{min}}$, to characterize the extent of delamination [58,76]. $\phi_{\text{min}}$ arises as a result of a separation of the coating and interfacial resistive-capacitive (RC) time constants. To explain whether changes of these coating property parameters with exposure time were caused by changes of delamination ratio $D$ or $\rho$ or both, Tsai and Mansfeld [58] rearranged the equations above and added new expressions for $f_{\text{min}}$ and $\phi_{\text{min}}$:

$$R_{po} = \rho \frac{d}{A_d} = \rho \frac{d}{D A} \quad (1-11)$$

$$f_b = K_b^0 \frac{D}{\rho} \left( K_b^0 = 1/(2\pi\varepsilon\varepsilon_0) \right) \quad (1-12)$$

$$f_{\text{min}} = a_4 \frac{D^{1/2}}{\rho} \left( a_4 = (2\pi d)^{1/4}(C_c^0/C_{dl}^0) \right) \quad (1-13)$$

$$\tan \phi_{\text{min}} = a_5 D^{-1/2} \left( a_5 = 2(C_c^0/C_{dl}^0)^{1/2} \right) \quad (1-14)$$

$$\frac{f_b}{f_{\text{min}}} = K_b^0 \left( a_4 \right)^{-1} D^{1/2} = (C_c^0/C_{dl}^0)^{1/2} (D)^{1/2} \quad (1-15)$$

$R_{po}$ and $f_b$ depend on the ratio $D/\rho$, but $f_b / f_{\text{min}}$ and $\tan(\phi_{\text{min}})$ depended only on $D$ with the assumption of constant $C_{dl}^0$ and $C_c^0$. Use of a combination of $f_{\text{min}}$ and $\phi_{\text{min}}$ provides a method for distinguishing between changes in coating defect resistivity and defect area. This approach is effective only for thin coatings. It is suggested that the probability of the change of $\varepsilon$, $\rho$ and $D$ with time should be considered when considering the use of $f_b$ for assessing coating performance [76].
Figure 1.11. The relationship between calculated break-point frequencies and the pore area [70].
1.4 REVIEW OF CORROSION DETECTION FOR AIRCRAFT

1.4.1 Background

The issue of corrosion damage in aging aircraft is receiving increasing attention in both military and commercial fleets as the early detection of corrosion in aging aircraft has both economic and safety implications. In airplanes, corrosion may occur in relatively inaccessible locations, such as deep within the lap joints of the fuselage [77]. As a result, detection of localized corrosion in a large, complex structure such as an airplane is extremely difficult. A variety of methods has been applied to corrosion detection and six are listed in Table 3. Most of these methods have been used in field corrosion detection for airplanes and show some promising results. However, only a limited area is sensed by methods due to the restriction of probe size, so these sensors (A-E) are only effective if they are physically located at the place where the corrosion is happening [78-82]. Detailed descriptions of these methods (A-E) are reviewed in references [82] [80,81] and are beyond the scope of this review.
<table>
<thead>
<tr>
<th>Methods</th>
<th>Theory</th>
<th>Application</th>
<th>Detection limit</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A). Thin film microsensor</td>
<td>Detect galvanic current</td>
<td>Real time, external and internal general corrosion</td>
<td>Limited area</td>
<td>Agarwala [79]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Pourbaix [83]</td>
</tr>
<tr>
<td>(B). Eddy current</td>
<td>Loss of conductive material detection</td>
<td>Periodically, Uniform corrosion</td>
<td>Limited area</td>
<td>Thompson [84]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Podney [85]</td>
</tr>
<tr>
<td>(C). Electrical Resistance (ER) Sensors</td>
<td>ER increase due to thickness loss of sensor</td>
<td>Real time, Uniform corrosion</td>
<td>Limited area</td>
<td>Ansuini [74]</td>
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<td>Stropki [86]</td>
</tr>
<tr>
<td>(D). Ultrasonic scanning</td>
<td>Detection of the thickness associated with reflecting wave time</td>
<td>Periodically, Uniform or localized corrosion</td>
<td>Limited area, Pixel size 0.05cm</td>
<td>Grills and Tsao [78]</td>
</tr>
<tr>
<td>(E). Magnetometer</td>
<td>Detection of magnetic field associated with corrosion current</td>
<td>Periodically, Uniform corrosion</td>
<td>Limited area,</td>
<td>Groner [77]</td>
</tr>
<tr>
<td>(F). Corrosion sensor coatings</td>
<td>Detection of pH change or oxidation state change</td>
<td>Uniform and localized corrosion, real time, Cumulative</td>
<td>Need the change of coating system</td>
<td>Johnson and Agarwala [87]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Johnson and Agarwala [88]</td>
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</tbody>
</table>

Table 1.3. Comparison of Six Corrosion Detection Methods
1.4.2 Corrosion sensing coating systems

The basic idea of a paint-sensor is to modify paint in order to make it a sensor for corrosion since paint covers, and thus has access to, the whole surface of a plane. The goal is to sense the oxidation process [80,81,87,89] or pH change associated with cathodic reaction that accompanies the oxidative corrosion reaction. The main cathodic reaction for any form of atmospheric corrosion is oxygen reduction, equation 1-1. For localized corrosion such as pitting and crevice corrosion, this cathodic reaction will tend to occur at more-accessible locations than the anodic reaction, i.e. nearer to the source of oxygen in the air. This reaction will cause an increase in the local pH at the location where it occurs, so a paint that is sensitive to pH increases generated by the cathodic reaction will indirectly be sensing corrosion occurring nearby.

pH indicators with color change properties have been used to sense corrosion and study the mechanism of corrosion in the well-known Evans water drop experiment [90]. Color-change pH indicators have also been incorporated into organic coatings as a tool for determining the pH gradients associated with filiform corrosion beads [30], Figure 1.12.

The indicators used for corrosion detection also include fluorescence compounds. Fluorescent dyes were applied to microelectronic test vehicles to detect pH changes associated with corrosion of Al or Au metallization under an applied bias in a humid environment [91]. Fluorescing and color-change dyes have also been applied to Al after corrosion in order to identify the locations of the hydrous aluminum oxide corrosion product [92]. Johnson et al. [87,88] have explored a number of selected Schiff-base compounds as potential fluorescence-based indicators for metal corrosion. Schiff-bases
such as 2, 6-disminoanthraquinone and 1,2-diaminoanthraquinone with salicylaldehyde.

are composed of a primary amine component and an aldehyde component, each of which
is attached to an aromatic backbone, and they are open to a wide range of functional
group substitutions. As a result of chelation reactions with metal ions generated by
anodic dissolution processes, such as Al, Ti and Fe, the Schiff-base chemicals could
produce strong fluorescence and thereby act as a corrosion sensor. Others [93] used
scanning electrochemical microscopy measurements in ferrocyanide and bromide
solutions, to locate active sites (pitting precursors) on polycrystalline Ti where oxidation
of Br- and Fe(CN)$_6^{4+}$ was possible.

Recently, Johnson and Agarwala incorporated into paint different chemicals that
fluoresce upon oxidation or upon complexation with metal cations formed by the
corrosion process [87-89]. The usefulness of the fluorescence compounds as indicators
of coating damage when incorporated, in their oxidized state, into a primer coating was
demonstrated [89]. A discontinuity in a topcoat that does not contain fluorescence
compounds would be revealed by the fluorescence of the underlying primer, Figure 1.13.

Such discontinuities represent sites where the risk of corrosion initiation is greatest, or
where the build-up of underlying voluminous corrosion products has led to coating
degradation. For the latter case, it was shown that fluorescence could be induced by the
complexing of aluminum ions generated in corrosion reactions with morin [87].
Figure 1.12. Filiform corrosion on aluminum under clear polyurethane with pH indicating primer after 47 days (a) microscopy photo (b) interpretation diagram [30].
Figure 1.13. Scribe shows fluorescence under UV light after corrosion damage; the painted panel contained fluorescein, a strong fluorescing compound. The color is actually yellow; it appears blue because of the UV light[87].
The focus of this thesis is the development and testing of coatings that are sensitive to the presence of underlying corrosion by detection of pH changes resulting from local pH increases associated with the accompanying cathodic reaction. This is accomplished by the addition of various pH-sensitive color-change or fluorescing compounds to different coating systems.

This thesis is organized into several sections, each of which was written as a stand-alone paper that either has been or will be submitted for publication. As a result, there is no single chapter on experimental methods; each of the chapters contains a subsection describing the relevant experimental approach. Similarly, each chapter contains abstract, introduction, results and discussion, and conclusion sections. The references have been separated out and can be found at the end of the thesis.

Chapter 2 is a paper that will be published in the October, 1999 issue of Corrosion. It describes the corrosion sensing behavior of modified acrylic coating systems. Modified acrylic coatings containing color-change or fluorescing compounds were determined to be sensitive to corrosion processes under the coatings by sensing the pH increase associated with the cathodic reaction. By applying constant cathodic current and measuring the charge at which color change or fluorescence was detected, the sensitivity of acrylic-based coating systems for detection of cathodic reactions associated with corrosion was determined. Visual observation of coated samples with the unaided eye can detect changes resulting from a charge corresponding to a hemispherical pit with depth on the order of 10 μm. The characteristics of modified acrylic coating systems
were studied by titration tests and demonstrated that different corrosion sensing ability were related with the critical pH value for modified paint that may not be same as pure indicators or fluorescing compound.

Chapter 3 describes further characterization of acrylic-based coatings by FTIR and Electrochemical Impedance Spectroscopy (EIS). EIS results indicated little influence of the indicating compound addition on the coating corrosion protectiveness. It was also demonstrated from EIS that the time for color change was determined to be controlled by the sensitivity of the coating to pH increase, and not by the coating protectiveness. FTIR showed that there was no structural change associated with the characteristic peak shift for the acrylic paint before and after modification by phenolphthalein, bromothylmol blue, or 7-hydroxycoumarin. The mixtures of indicator and polymer apparently resulted only in physical blending.

In chapter 4, a new corrosion detection method is introduced, which uses modified agar-gel as a corrosion sensing medium. Color-change indicators or fluorescing compounds that are sensitive to pH were added to the agar gel. This coating would be temporary in nature, applied only to find the location of corrosion and then removed. The formation and structure of the modified agar-gel upon addition of pH indicators or fluorescing compounds are discussed. Corrosion sensing behavior associated with the time for initial color change or fluorescing was demonstrated to be dependent on gel composition, corrosion initiation conditions, and surface conditions before applying the gel coating.

Chapter 2 and 3 present work on acrylic based coatings. However, acrylic primers are not used on airplanes. A typical aerospace primer is epoxy-polyamide. In
order to determine if the approach developed with acrylic paint could be applied to airplanes, experiments were performed on epoxy polyamide systems, and the results are given in Chapter 5. Several selected pH indicators or fluorescing compounds were incorporated into epoxy polyamide paint. Color change or fluorescing behavior was studied and is discussed in terms of the intrinsic pH value of two components of epoxy. The corrosion sensing behavior has been determined and the results were explained by the pH sensing properties of modified epoxy paint from titration experiments. Results showed that color change pH indicators can be used to modify the epoxy coating to sense the cathodic reaction as long as the overall pH value was adjusted to below the critical pH value of color change for pH indicators. The fluorescing interference from both the resin and hardener components made it difficult to use fluorescence compounds for corrosion detection. Corrosion sensing properties of modified EP coating after dilution have been shown to depend on the pH sensing behavior of modified coating systems. Indicator-containing epoxy coatings formed with neutralization and dilution appear to be promising candidates as effective corrosion sensing primer coatings.
CHAPTER 2

INVESTIGATION OF THE CORROSION SENSING BEHAVIOR OF
AN ACRYLIC BASED COATING SYSTEM

ABSTRACT

Paint systems containing color-change or fluorescing compounds were found to be sensitive to underlying corrosion processes by reacting to the pH increase associated with the cathodic reaction that accompanies corrosion. The sensitivity of acrylic-based coating systems for detection of cathodic reactions associated with corrosion was determined by applying constant cathodic current and measuring the charge at which color change or fluorescence was detected. Visual observation of coated samples with the unaided eye can detect changes resulting from a charge corresponding to a hemispherical pit with depth on the order of 10 μm. The characteristics of modified acrylic coating systems were studied by titration tests. Electrochemical Impedance Spectroscopy was also performed to test the influence of the indicating compound addition on the coating corrosion protectiveness. The time for color change was
determined to be controlled by the sensitivity of the coating to pH increase, and not by the coating protectiveness.

2.1 INTRODUCTION

The early detection of corrosion in aging aircraft has both economic and safety implications. In airplanes, corrosion may occur in relatively inaccessible locations, such as within the lap joints of the skin of an airplane [77] as is shown schematically in Figure 2.1. As a result, detection of localized corrosion in a large, complex structure such as an airplane is extremely difficult. Many different sensors and techniques are being developed to detect corrosion. [80,83,85] However, these sensors are only effective if they are either physically located at the place where the corrosion is happening, or sensitive to corrosion occurring remotely.

The basic idea of this study is to modify paint in order to make it a sensor for corrosion since paint covers, and thus has access to, the whole surface of an airplane. The goal is to sense the cathodic reaction that accompanies the oxidative corrosion reaction. The main cathodic reaction for any form of atmospheric corrosion is oxygen reduction:

\[ \text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^- \]  

(2-1)

For localized corrosion such as pitting, crevice, and exfoliation corrosion, this cathodic reaction will tend to occur at more-accessible locations than the anodic reaction, i.e. nearer to the source of oxygen in the air, Figure 2.1. This reaction will cause an increase
in the local pH at the location where it occurs, so a paint that is sensitive to pH increases generated by the cathodic reaction will indirectly be sensing corrosion occurring nearby.

Others have pursued similar approaches. Color-change pH indicators have been incorporated into organic coatings as a tool for determining the pH gradients associated with filiform corrosion beads [30]. Fluorescent dyes were applied to microelectronic test vehicles to detect pH changes associated with corrosion of Al or Au metallization under an applied bias in a humid environment [91]. Fluorescing and color-change dyes have also been applied to Al after corrosion in order to identify the locations of the hydrous aluminum oxide corrosion product. More recently, Johnson and Agarwala incorporated into paint different chemicals that fluoresce upon oxidation or upon complexation with metal cations formed by the corrosion process [79,88,89].

The present work focuses on various coating systems with an acrylic-based organic matrix and different indicating compounds that can be used to sense the pH change associated with the corrosion process. The sensitivity of these coating systems for detection of cathodic reactions associated with corrosion was determined by applying constant cathodic current densities and measuring the charge at which color change or fluorescence was detected. Electrochemical Impedance Spectroscopy was also performed after different immersion times in 1 M NaCl solution to test the influence of the indicating compound addition on the coating corrosion protectiveness.
Figure 2.1. Schematic drawing of crevice corrosion in a painted lap joint. Al dissolution/corrosion happened inside the crevice formed by fastener Al sheet while oxygen reduction reaction occurred at the location of coating defects outside of crevice. The reactions in the figure indicate the type of half electrochemical reactions.
2.2 EXPERIMENTAL

2.2.1 pH Sensing Coating Systems

Clear acrylic paint (ECS-8 paint from Tru-Test Mfg. Co., Cary, IL) was mixed with different color-change (phenolphthalein or bromothymol blue) or fluorescing (7-hydroxycoumarin or coumarin) pH indicators. Color change can be easily observed through the transparent acrylic matrix. These indicators were chosen as additives because the pH ranges over which they change color are in the alkaline region, e.g. 8.2-10 for phenolphthalein and 6-7.6 for bromothymol blue. The indicators were added at concentrations from 0.1 to 2.4 wt%, which is the saturation concentration for phenolphthalein in acrylic. Both 7-hydroxycoumarin and coumarin are fluorescent acid-base indicators with pH ranges for fluorescing of 6.5-8.0 and 9.5-10.5, respectively [94].

The indicating layers were coated by cotton swab on the surface of Al alloy samples that were previously mounted in epoxy and polished to #600 grit emery paper, and the coating thickness was controlled by the number of swab applications. These samples were then top-coated with a uniformly-sprayed clear acrylic (containing no indicating compounds), Figure 2.2. The combined thickness of the two layers was about 10-20 μm. Color change was monitored with the unaided eye. Incident UV radiation from a UV lamp (UVP Inc.) with a major peak wavelength of 365 nm was used for the systems containing fluorescent compounds.

The critical pH value for color change or fluorescence was determined by titration using various coatings applied on glass slides. The samples were immersed in stirred DI water and drops of 0.01, 0.1 or 1 M NaOH solution were added. The pH was recorded
Figure 2.2. Schematic drawing of coating systems used in this study. The modified coating (pH indicators or fluorescing compounds plus polymer paint matrix) was sandwiched between the Al substrate and topcoat.
and the sample surface was monitored for color change or fluorescence. The effect of curing time on the color change or fluorescence response was determined for several modified acrylic-based coating systems. The time for initial color change or fluorescence was measured for coatings on glass slides in two or three selected pH solutions after various curing times.

2.2.2 Galvanic corrosion tests

For galvanic corrosion tests, a 4 mm diameter copper rod was inserted into a 5.5 mm diameter hole in an Al 2024 sample, but kept electrically isolated by filling epoxy in between. The sample was mounted and polished to reveal a section of the rod in the alloy. The various pH sensitive coatings were applied on the polished surface. The sample was immersed in 1M NaCl solution and the galvanic current was measured using a zero-resistance ammeter (Gamry Instruments PC3 with CMS 100 measurement software).

2.2.3 EIS characterization of acrylic-coated sample

Electrochemical Impedance Spectroscopy (EIS) has been used widely to evaluate the resistance of coated metals to corrosion [70,71,95,96]. In this study, EIS was performed on different types of acrylic-phenolphthalein indicating coatings using the Gamry Instruments EIS 900 system. The indicator content in the acrylic-based paint was 0.5 or 2.4 wt%, and one or two indicating coating layers were applied, corresponding to a total coating thickness of about 15 and 30 μm, respectively. For the 2.4 wt% phenolphthalein content acrylic indicating coating, additional tests were performed on
samples with an extra topcoat layer of pure acrylic having a thickness of about 10 μm. Two or three samples were fabricated and tested for each case. Also, as control experiments, samples coated with pure acrylic were tested by EIS at different immersion times. EIS tests were performed at prolonged immersion times in 1M NaCl, including the time for initial color change of the corrosion sensing coating. The EIS experimental parameters were as follows: frequency range 0.01 to 10,000 Hz, 10 pts per decade, and ±10 mV potential amplitude relative to the open circuit potential. Immersion cells were covered completely to minimize evaporation during the immersion period. The initial color change time was monitored by visual inspection.

2.3 RESULTS AND DISCUSSION

2.3.1 Characteristics of the Sensing Coatings

The first task in this study was to determine if the approach of using paint to sense corrosion is reasonable, and several preliminary experiments were performed. Samples of Al alloy AA 5454 were coated with different coating systems and immersed in 1 M NaCl. After a certain immersion time, colored spots were seen to appear, Figure 2.3 (a, b). The dark spots seen in Figure 2.3 are defects in the coating, and not pits. The colored spots that developed were red and blue for acrylic-based coatings containing phenolphthalein and bromothymol blue, respectively. This suggested that the spots of color change were, in fact, the sites of increased pH associated with the cathodic reaction.
Figure 2.3. Photographs of color change of two pH sensing coatings on Al 5454 substrate following immersion in 1.0 M NaCl solution. (a). phenolphthalein paint after 8 days
Figure 2.3 Continued

Figure 2.3. Photographs of color change of two pH sensing coatings on Al 5454 substrate following immersion in 1.0 M NaCl solution. (b). phenolphthalein paint after 8 days.
of the local attack of the coated Al alloy in the chloride solution. As will be shown below, a volume of corroded material equivalent to a 15 \( \mu m \) radius pit will generate sufficient charge to create a color-change spot. Furthermore, the surface of a sample abraded to 600 grit is relatively rough. Therefore, it is not possible to find the corroded area responsible for a small color-change spot by microscopic examination. However, as shown in Figure 2.4 (a), the initial color change spots do tend to be associated with polishing scratches, which may be sites for the initiation of localized attack. After extended immersion times, pits are clearly seen to develop near red-colored regions, Figure 2.4 (b), 2.4 (c). It should be noted that the red spot on the left side of Figure 2.4 (c), which is separated from the pit by about 200 \( \mu m \), may be related to a pit that is out of the frame of the photograph.

In order to demonstrate further that the initial color change of the sensing coating is associated with corrosion processes, the same coating was applied to the surface of a highly polished sample (to 3 \( \mu m \) diamond paste) and the sample was immersed in 1 M NaCl solution. The sample surface was observed by optical microscopy at magnifications of up to 1000x at 5 min intervals. Red color change spots could be observed after only 20 min immersion, and pits were clearly associated with these red spots, Figure 2.5 (a), 2.5 (b). The roundish features on the surface in Figure 5 were also present before solution exposure. Examination of these features by atomic force microscopy indicated that they were about 10-20 \( \mu m \) in diameter and protruded from the surface by about 1-3 \( \mu m \), Figure 2.6. Such features are not found on surfaces abraded to
600 grit prior to coating. It is assumed that they form as a result of lower surface tension at the interface of the acrylic and the highly polished sample surface.

In order to check the assumption that a remote cathodic reaction associated with crevice corrosion could be detected, an artificial crevice cell was assembled as shown in Figure 2.7. Two pieces of alloy 2024 were mounted in epoxy, one concentric to, but isolated from, the other. After polishing and coating with an acrylic/phenolphthalein (2.4%wt) sensing system, the sample was clamped between two solid acrylic sheets so that the entire inner electrode and part of the outer electrode were covered. The assembly was immersed in 1 M NaCl and a potential of 500 mV was applied between the two electrodes such that the current flowing to the inner electrode was positive. This design simulated crevice corrosion by having a buried local anodic site surrounded by cathodic area that was partially buried. After 4 h, a clear uniform red color developed on the portion of the outer cathodic electrode that was not covered by a solid acrylic sheet, Figure 2.8 (a). The ohmic potential drop associated with current flow to buried regions of the outer electrode resulted in most of the current flowing to the uncovered part of that electrode. After 26 h, the color change could be clearly seen in the upper right corner beyond the dashed line in Figure 2.8(b). After this extended immersion time, several pits formed on the outer part of this electrode despite the applied cathodic current. These pits may have been regions of cathodic corrosion, to which Al alloys are susceptible [97]. Nonetheless, the fact that the cathodic current flowed to the exposed cathodic area validates the approach of using a sensing coating system to detect the cathodic reaction associated with buried crevice corrosion.
Figure 2.4 (a). Optical Micrographs of Al 2024 T3 coated with acrylic-phenolphthalain (2.4wt%) after immersion in 1 M NaCl for (a) 4hr.
Figure 2.4 Continued

Figure 2.4 (b). Optical Micrographs of Al 2024 T3 coated with acrylic-phenolphthalein (2.4wt%) after immersion in 1 M NaCl for 9hr.
Figure 2.4. Optical Micrographs of Al 2024 T3 coated with acrylic-phenolphthalein (2.4wt%) after immersion in 1 M NaCl for (c) 8 days.
Figure 2.5. Optical Micrographs of highly polished Al 2024 T3 coated with acrylic-phenolphthalein (2.4wt%) after immersion in 1 M NaCl for (a) 20 min. The arrows indicate the pitting sites.
Figure 2.5 Continued

Figure 2.5. Optical Micrographs of highly polished Al 2024 T3 coated with acrylic-phenolphthalein (2.4wt%) after immersion in 1 M NaCl for (b) 1hr. The arrows indicate the pitting sites.
Figure 2.6. AFM topographic map (a) and line scan (b) for an Al 2024 T3 sample coated with acrylic - phenolphthalein (2.4wt%) (20-30 μm thickness)
Figure 2.7. Schematic drawing of artificial crevice assembly. Two pieces of AA 2024-T3 were mounted in epoxy, one concentric to but isolated from the other. The inside sample and part of outer sample were confined within the crevice formed between plastic sheet and sample surface. Cathodic current was passing through outer sample by applying 500 mV potential.
Figure 2.8. Photograph of artificial crevice sample with acrylic/phenolphthalein (2.4 wt%) coating after applying constant potential of 500 mV for (a) 4 hrs.
Figure 2.8. Photograph of artificial crevice sample with acrylic/phenolphthalein (2.4 wt\%) coating after applying constant potential of 500 mV for (b) 26 hr in 1 M NaCl solution. Above dotted line was not under the crevice covering.
The critical pH values for color change or fluorescence of various compounds are well known [94]. However, the values may change when these compounds are mixed with an organic matrix and applied to a surface. In order to determine the critical pH values of the coatings, titration tests were performed on samples consisting of glass slides coated with the sensing paint, but no topcoat. These samples were immersed in deionized water, and NaOH was slowly added while monitoring the solution pH until a color change on the sample was observed. The results are given in Table 2.1. It was found that the acrylic/phenolphthalein coating and acrylic/bromothymol-blue coating (both with 2.4 wt% indicator content) had almost the same critical pH value for color change of about 10. Note that this value is well above the range of critical pH value for color change for pure bromothymol blue. The critical pH value for the coating containing the fluorescing compound 7-hydroxycoumarin was much lower than that with other pH indicators. It is clear that the pH values for color change or fluorescence of these compounds are not necessarily the same after they are mixed with organic paint matrices. In order to confirm the change in critical pH value after mixing pH indicators with acrylic, another commercial blue-tinted Al primer (#1200 from Tru-Test Mfg Co, Cary, IL), which contains acrylic resin, mineral spirits, glycol ethers and ethyl acetate, was tested as a matrix containing pH indicators. Titration test results showed the same deviation from the critical pH values of pure compounds, Table 2.1.

The effect of room temperature curing time on the time at which initial color change or fluorescing behavior occurred was measured for modified acrylic coating systems (containing 2.4 wt% phenolphthalein, 0.5 wt% 7-hydroxycoumarin, or 2.4 wt% bromothymol blue) on glass slides in constant pH value solutions. Two or three solution
pH values were selected starting from the critical pH value from the titration tests and stepping up 1.5 or 2 units. The results are shown in Figures 2.9 (a-c). Acrylic-7-hydroxycoumarin coatings systems exhibited shorter and stable initial fluorescing times, as shown in Figure 2.9 a, while the acrylic modified by phenolphthalein or bromothymol blue showed either strong curing dependence or much longer time for color change (approximately 100 times longer than acrylic-7-hydroxycoumarin systems), Figures 2.9 b and c. Since this color change or fluorescing time also determined the pH sensing behavior for the modified coatings, the correspondence among results from time-curing testing, titration testing and sensitivity testing (discussed below) confirm the relationship between pH sensing behavior and corrosion sensitivity.

<table>
<thead>
<tr>
<th>pH indicators</th>
<th>Fluorescing compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pheno</td>
<td>Bromo</td>
</tr>
<tr>
<td>pure compound</td>
<td>8.2-10</td>
</tr>
<tr>
<td>clear acrylic</td>
<td>10</td>
</tr>
<tr>
<td>1200 primer</td>
<td>9-12.5</td>
</tr>
</tbody>
</table>

Table 2.1. pH value for color change or fluorescence for pure compounds (from ref. [94]) and for compounds mixed into organic coatings
Figure 2.9 (a). The dependence of time for initial color change or fluorescing behavior under UV radiation on curing for modified acrylic coating system with (a) 0.5 wt% 7 hydroxycoumarin.
Figure 2.9 (b). The dependence of time for initial color change or fluorescing behavior under UV radiation on curing for modified acrylic coating system with (b) 2.4 wt% phenolphthalein.
Figure 2.9 (c). The dependence of time for initial color change or fluorescing behavior under UV radiation on curing for modified acrylic coating system with (c) 2.4 wt% bromothymol blue.
2.3.2 Sensitivity Determination

It is of interest to determine the sensitivity of the various coating systems to corrosion, i.e. how much corrosion is required before a color change is observed. One way to do this is simply to measure the time for the first sign of observable color change at open circuit in a certain solution. Figure 2.10 shows the time for initial color change for phenolphthalein-containing coatings on AA2024-T3 immersed at open circuit in 1 M NaCl. Color change is observed sooner as the phenolphthalein content increases. This decrease in time for color change could be attributed to two separate factors: increased sensitivity of the coating to pH change, or decreased protectiveness of the coating leading to faster corrosion. It is therefore important to determine both how much corrosion is needed for observable color change for each coating system independent of the coating protectiveness, and also to measure the protectiveness of each coating independent of its color change ability. As described below, a new sensitivity test was developed for the former, and EIS was used to test the latter property.

Since the system senses corrosion by detecting the pH change associated with the cathodic reaction, one measure of the sensitivity of the coatings can be assessed by impressing a cathodic current on the metal and determining the time for color change. The sensitivity to pH change at the coating/metal interface is determined independent of the protectiveness of the coating because the cathodic current is forced. Constant cathodic current densities were applied to samples of the type shown in Figure 2.2 (i.e. not in the artificial crevice cell) in 1M NaCl solution. The samples were immersed in the solution for 10 minutes before each test. The time of the initial color change or
Figure 2.10. The relation between phenolphthalein content and time for initial color change for different Acrylic-phenolphthalein systems. OC refers to open circuit.
fluorescence as determined by the unaided eye was measured for each value of applied current density.

Since current density, $i$, is defined as $q/t$, where $q$ is charge density and $t$ is time, the following relationship should exist between the elapsed time until detection of color change, $t_{DET}$, the charge density passed at detection, $q_{DET}$, and the applied current density, $i_{APP}$:

$$\log t_{DET} = \log q_{DET} - \log i_{APP} \quad (2-2)$$

Therefore, a plot of $\log t_{DET}$ vs. $\log i_{APP}$ should have a slope of -1, and an intercept that provides a value of detectable charge density, which is a measure of the sensitivity. The data for the acrylic/phenolphthalein (2.4%wt) indicator coating as well as a fit to Eqn. 2-2 are shown in Figure 2.11. The detectable charge density is found to be $5.26 \times 10^{-4}$ C/cm$^2$. Assuming that this amount of charge was generated from a single hemispherical pit, the radius (or depth) of the pit, $r$, can be calculated from Faraday's law:

$$r(cm) = \left( \frac{3 q_{DET} A_{CATH} M}{2\pi \rho 0.8 nF} \right)^{1/3} = 2.74 \times 10^{-2} (q_{DET} A_{CATH})^{1/3} = 2.2 \times 10^{-3} A_{CATH}^{1/3} \quad (2-3)$$

where $A_{CATH}$ is the area over which the cathodic reaction is occurring in cm$^2$, $M$ is the effective atomic weight of the alloy (close to 27 g/mole for Al alloys), $\rho$ is the alloy density (close to 2.7 g/cm$^3$ for Al alloys), $n$ is the charge on the dissolved metallic ion (3
Figure 2.11. Detection time for color change vs. applied cathodic current density for Al 2024 alloy coated with acrylic/phenolphthalein coating in 1 M NaCl solution.
Figure 2.12. Effect of specimen area on the detection time for Al 2024 alloy coated with acrylic/phenolphthalein (2.4%wt) coating under constant current density of 5 μA/cm² in 1.0 M NaCl solution.
for Al), and F is Faraday's constant. It is also assumed in Eqn. 2-3 that 20% of the
anodic charge in the pit would be consumed locally by hydrogen evolution in the pit [98].

The time for color change in the galvanostatic experiments summarized in Fig. 2.10 varied over a wide range depending on the applied current density. Figure 2.10 shows that the time for color change at open circuit for the 2.4% phenolphthalein coating was about 5 h, which is longer than the time required for every value of applied cathodic current except the lowest, $10^{-8}$ A/cm$^2$. At this very low applied cathodic current density, the time for color change was about 28 h, which is significantly longer than the time required at open circuit. This finding may be caused by a reduction in pitting due to cathodic protection and resulting differences in local current distribution.

It is obvious from Eqn. 2-3 that the size of a detectable “effective” pit should be related to the size of the cathodic area. In other words, if the anodic charge associated with a pit is spread over a larger cathodic area, more charge (more time, or a larger “effective” pit) would be required to cause a color change. However, there is a problem with the analysis presented above. According to Eqn. 2-2, the detection time should be independent of sample area for a constant value of applied cathodic current density. Figure 2.12 shows the effect of sample area on the sensitivity measurement for the acrylic/phenolphthalein system with an applied cathodic current density of 5 $\mu$A/cm$^2$. It is clear that the detection time decreases with increasing sample area, in contrast to the expectations of the model. Another way to approach this discrepancy is to measure the detection time for different sample areas using a fixed applied current instead of a fixed current density. For a fixed current, $I_{\text{APP}}$, the time for detection in the sensitivity experiments should vary with the sample area according to:
Figure 2.13 shows the effect of sample area on the detection time with a constant applied cathodic current of 5μA, as well as the relationship expected from Eqn. 4 using the previously-determined value of $q_{DET}$. The experimental data matched the expected values well when the area was less than 1.2 cm$^2$. For larger sample areas, however, the measured detection times were smaller than the expected values.

Another interesting observation was that the initial color change that occurred in these experiments happened at small spots rather than uniformly over the whole area. These spots of color change appeared at essentially the same time. This localized effect also occurred during corrosion at open circuit, as shown in Figure 2.3. The applied current will not flow uniformly to the electrode surface, but will instead tend to flow to the defective areas in the coating. This is also the case in a real coated crevice. Since a larger sample area will statistically be more likely to have severe defects, the time for detection will actually decrease rather than increase with increasing sample area. These observations must be taken into account, and the analysis can be improved as described presently.

Consider that the current flowing to a given coated sample is distributed among N defective points. The charge passed at the point of detection is then a total charge, $Q_{TOT}$, which is equal to ($N \times Q_{DET}$), where $Q_{DET}$ is the critical charge required for detection of each single spot. The previous analysis can thus be modified:
Figure 2.13. Comparison between experimental and expected relationships of detection time and sample area for Al 2024 alloy coated with acrylic/phenolphthalein (2.4%wt) coating with applied cathodic constant current of 5μA.
Figure 2.14. Sensitivity test results for acrylic/phenolphthalein (2.4%wt) indicator coating system in 1 M NaCl solution.
\[ I_{\text{APP}} = \frac{Q_{\text{TOT}}}{t_{\text{DET}}} = \frac{(Q_{\text{DET}}N)}{t_{\text{DET}}} \quad (2-5) \]

\[ \log \left(\frac{t_{\text{DET}}}{N}\right) = \log Q_{\text{DET}} - \log I_{\text{APP}} \quad (2-6) \]

According to this analysis, a plot of \( \log \left(\frac{t_{\text{DET}}}{N}\right) \) vs. \( \log I_{\text{APP}} \) should have a slope of -1, and an intercept that provides a value of detectable charge, \( Q_{\text{DET}} \). Figure 2.14 shows the data replotted in this fashion, along with a fitted line with slope -1. \( N \) was taken to be the number of the first color change spots to appear. The scatter of the data points at a given applied constant current in Figure 2.14 reflects the reproducibility of the measurement. From the intercept in Figure 2.14, \( Q_{\text{DET}} \) can be determined to be \( 1.22 \times 10^{-4} \) C. The form of Faraday's law shown in Eqn. 2-3 needs to be altered to consider the detection charge instead of charge density:

\[ r(\text{cm}) = \left(\frac{3}{2\pi} \frac{Q_{\text{DET}} M}{0.8 \rho_{\text{F}}} \right)^{1/3} = 2.74 \times 10^{-2} (Q_{\text{DET}})^{1/3} \quad (2-7) \]

This "effective" pit size is independent of the cathodic area, but dependent on the number of defects, \( N \), since the intercept in plots like Figure 2.14 will be dependent on \( N \). Using the value for \( Q_{\text{DET}} \) of \( 1.22 \times 10^{-4} \) C, the size of an effective detectable pit with the acrylic/phenolphthalein system was then 13.6 \( \mu \text{m} \). The detectable pit depth determined in this fashion was used in this study as a measure of the sensitivity of the indicating coating systems. A small detectable pit depth is thus associated with a highly sensitive
coating. This approach to determination of the sensitivity of these coating systems to underlying corrosion suggests that a very small amount of corrosion can be detected.

A slightly different y-axis intercept is found using the line determined by an unconstrained least squares fitting. However, the relationship between charge and current, Eqn. 2-6, demands the slope be $-1$. Furthermore, the detectable pit depth determined from Eqn. 2-7 is weakly dependent on $Q_{DET}$ because of the $1/3$ power, so the use of an unconstrained least squares fit would have little effect on the final result.

Following the method discussed above, the sensitivities of different sensor coating systems were determined, and the results are presented in Table 2.2. It should be noted that different ranges of applied constant cathodic current were used for the different coating systems due to the differences in color change or fluorescence response. The results in Table 2.2 are well-correlated with the critical pH values determined for the different systems, which were given in Table 2.1. The sensitivity of the acrylic-based systems with phenolphthalein and bromothymol blue were similar (and probably within the error of the analysis), which corresponds to the fact that the critical pH determined from titration for these two systems was identical. The acrylic-based coating with 7-hydroxycoumarin was much more sensitive as it exhibited a very small detectable pit size. Furthermore, the sensitivity increased (detectable pit radius decreased) as the 7-hydroxycoumarin content increased to 0.5 wt%. The response of this system was extremely long-lived compared to other systems. The fluorescent spots could easily be seen for long periods of time (several hr to several days, depending upon the charging conditions) after the cessation of the cathodic current and removal from solution. In contrast, the systems with phenolphthalein reverted back to colorless after less than 1 hr
following the cathodic treatment and removal from solution. This fading took somewhat longer, about 12 h, following long term immersion in chloride solution at open circuit. It is therefore clear that the critical pH values of the organic/indicator mixtures have a strong effect in determining the sensitivity of the coating system for corrosion detection.

During experiments where 2024-T3 was galvanically coupled to a piece of Cu and covered with an acrylic-phenolphthalein coating (2.4 wt%), color change only occurred on the surface of copper sample where the cathodic reaction predominated. The critical charge at the time of initial color change can be calculated from integration of the measured current by the ZRA. This charge can be converted to an effective pit size in order to get coating sensitivity. For the acrylic-phenolphthalein (2.4 wt%, two layer) coating, the effective observable pit size determined from the galvanic corrosion experiment was found to be 7.5μm, which corresponds well to the results from the constant cathodic current sensitivity tests (7.9 μm). This suggests that the galvanostatic approach for sensitivity used in this study for accelerated testing is reasonable.

<table>
<thead>
<tr>
<th>Organic Matrices:</th>
<th>Acrylic Phenolphthalein</th>
<th>Acrylic Bromo.</th>
<th>Acrylic 7-hydroxy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Indicator</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Topcoat (acrylic)</td>
<td>with</td>
<td>w/o</td>
<td>with w/o w/o</td>
</tr>
<tr>
<td>Content (%wt)</td>
<td>2.4</td>
<td>2.4 (two layer)</td>
<td>2.4 0.1 0.5</td>
</tr>
<tr>
<td>Time for initial color change(hr)</td>
<td>5.2</td>
<td>0.94</td>
<td>5.5 0.78 0.31</td>
</tr>
<tr>
<td>Effective Pit Radius (μm)</td>
<td>13.6</td>
<td>7.9</td>
<td>12.7 4.9 2.02</td>
</tr>
</tbody>
</table>

Table 2.2 Comparison of corrosion sensing behavior of different modified organic paint
Figure 2.15. The approximately linear relationship between the time for initial color change or fluorescence and calculated effective pit depth for acrylic-phenolphthalein and acrylic-7 hydroxycoumarin sensing coating systems immersed in 1M NaCl solution.
A comparison of the time for initial color change at open circuit to the effective
detectable pit radius determined by the galvanostatic sensitivity test is given in Figure
2.15 for a range of coating systems. It is clear that there is a correlation between the two
values of sensitivity, which were measured in totally different fashions. The time for
initial color change at open circuit is influenced by both the protectiveness of the coating
and the sensitivity of the material to pH increase. The galvanostatic test, however,
implies a current, and is thus independent of the coating protectiveness. The correlation
of the two values suggests that the time for initial color change is not determined by
coating protectiveness, but rather by the sensitivity to pH change.

2.3.3 EIS Experiments

The protectiveness of the coatings can be determined independent of their
sensitivity to pH using EIS. The EIS data were fitted to the equivalent electrical circuit
shown in Figure 1.6 (b) using the Z-View program. Breakpoint frequency values, \( f_b \),
were also determined from the EIS data and were used to calculate values of pore
percentage according to methods described in the literature \([64,66,76,99]\). An example of
a fit obtained in this fashion is shown in Figure 2.16. For acrylic-based coatings on Al
2024 alloy, it was found, as expected, that the coating and double layer resistance
decreased, and the coating and double layer capacitance increased, with increasing
immersion time in 1M NaCl. Values of \( S/S^0 \), the pore percentage, and low-frequency
modulus, are given in Figure 2.17 as a function of color change time at open circuit for a
variety of coating systems. The EIS spectra were collected at the time of initial color
change.
For coating systems with times for initial color change of less than 4 h (the most sensitive coating systems), the pore percentage, $S/S^0$, decreases and high low-frequency impedance, $Z_{lf}$, increases as the open circuit color change time decreases, Figure 2.17. Coating pore resistance and charge transfer resistance also vary with color change time in this range. The pore percentage and various equivalent circuit parameters do not change further for coating systems having color change time longer than about 4 h. (Note that the pore percentage calculation is limited at 20% because of the limited frequency range of measurement.) The relationship of time for color change at open circuit and corrosion sensitivity from the galvanostatic approach, Figure 2.15, indicated that short times for color change were not a result of low coating protectiveness. The coatings with the shortest color change time actually had the highest low-frequency impedance and the lowest pore percentage. The relationships of $S/S^0$, effective detectable pit radius and time for initial color change verify the breakpoint frequency theory [64,76,99]. It is possible that the decreased time for color change associated with the most-protective coatings is a result of effective trapping of the solution in the pores compared to the less protective coatings.
Figure 2.16. EIS data (points) and fit to equivalent circuit (lines) for acrylic coating (about 30μm) on Al 2024 after immersion for 19hr in 1M NaCl solution. The breakpoint frequency and low frequency impedance, $Z_{lf}$, are marked by the arrows, which determined by the frequency at phase shift of $45^\circ$ and impedance at the lowest frequency measured respectively.
Figure 2.17. Relationship between $t_r$, $Z_{lf}$ and $S/S^0$ for acrylic-phenolphthalein coatings on AA 2024-T3 in 1M NaCl. The shortest color change time corresponds to small pore percentage and high low frequency impedance.
2.4 CONCLUSIONS

The viability of using modified paint systems to detect hidden crevice corrosion in the underlying metal was studied in this work. The approach was to add a pH-sensing compound to detect the pH increase associated with the cathodic reaction that accompanies the anodic corrosion reaction. Different combinations of organic matrix and indicating compounds were studied. Titration experiments, sensitivity tests, EIS, and electrochemical DC techniques have been applied to characterize the modified corrosion sensing coating systems. The following conclusions can be made:

1. Color change or fluorescence associated with the pH increase caused by the cathodic reaction in the corrosion process was easily seen with the unaided eye.
2. The critical pH for color change or fluorescence changed when an indicating compound was mixed with an organic matrix.
3. The time for observable initial color change at open circuit decreased as the concentration of pH indicator in the coating system increased.
4. The sensitivity of these coating systems was determined by passing constant cathodic current and determining the charge at which color change or fluorescence was detected. This was related to the radius of an effective pit. Pit sizes on the order of 10 μm were found to be detectable by the unaided eye with the coating systems studied.
5. The time for observable initial color change at open circuit was proportional to the effective detectable pit radius determined from the constant current experiments.
5. Coatings with short times for observable initial color change at open circuit exhibited high low-frequency impedances and low pore percentage, as calculated from the breakpoint frequency.

6. The time of initial color change at open circuit was determined to be dependent on the pH sensitivity of the coating, and not the coating protectiveness.

7. Since the method for determining the sensitivity used observation by the naked eye, the values of sensitivity in terms of detectable pit depth may not be absolutely accurate, and could decrease if magnification were used. However, the comparison of detection ability for different sensing coating systems is meaningful and this approach itself is promising for further improvement.
CHAPTER 3

FTIR AND EIS ANALYSIS OF CORROSION SENSING COATING

ABSTRACT

Corrosion sensing coatings developed previously were characterized by Fourier Transform Infra-Red (FTIR) and Electrochemical Impedance Spectroscopy (EIS). EIS results showed that the indicating compound addition had little effect on the coating corrosion protectiveness. It was suggested by FTIR that no structural changes occurred in the acrylic paint before and after modification by phenolphthalein, bromothylmol blue, and 7-hydroxycoumarin. The conclusion can be made that the addition of indicators or fluorescing compound did not produce significant structural changes. The mixture of indicator and polymer apparently results only in physical blending.
3.1. INTRODUCTION

The early detection of corrosion in airplanes has become a major concern and has stimulated considerable research [77,82,100]. One approach has been to develop corrosion sensing paint systems as mentioned in the previous chapter. An understanding of the structure of the modified paint/coating is of considerable interest in order to explain the critical pH value associated with corrosion sensing ability of the paint. Fourier Transform Infrared Spectrometry (FTIR) is currently in wide use for the study of the chemical structure of polymeric paints [101-112]. FTIR can provide understanding regarding the chemical interaction between the polymer matrix and indicator additives, which is important for improving the understanding of modified coating systems. In this study, acrylic paint was examined by FTIR before and after modification with various chemicals, consisting of three different pH indicators at the same concentration as used in the previous work. The curing processes were also studied through characteristic bonding analysis of FTIR spectra.

Electrochemical Impedance Spectroscopy (EIS) has been successfully applied to the study of different kinds of corrosion such as general corrosion [44], localized corrosion (pitting) [44-47], stress corrosion cracking [48], corrosion in low conductivity media [39], and corrosion under coating systems [49,51,67]. The most successful application of EIS has been in the evaluation of the corrosion behavior of polymer coated metals [37,38]. In this work, EIS tests were performed after prolonged immersion times in 1M NaCl, including the time for initial color change of the corrosion sensing coating.
Coating properties such as resistance, capacitance, and water uptake have been explored and correlated with corrosion sensing behavior of modified coating system.

3.2. EXPERIMENTAL

3.2.1. FTIR analysis of corrosion sensing paint

FTIR spectra were collected for the modified paint and coating using a Bruker Equinox 5S IR microscope. Clear acrylic paint (ECS-8 paint from Tru-Test Mfg Co, Cary, IL) was mixed with several selected pH indicators such as phenolphthalein (0.1, 0.5, 2.4 wt%), bromothymol blue (0.1, 0.5, 2.4 wt%) or a fluorescing compound e.g. 7-hydroxycoumarin (0.1, 0.5, 1.0 wt%) (from Aldrich Chemical Co.). The mixture was cast on a KBr tablet, used as a sample holder to minimize spectrum noise. The wave number was scanned in the mid-IR range between 400 to 4000 cm\(^{-1}\) with a resolution of 4 cm\(^{-1}\). Both uncured and cured paints were analyzed, as well as pure indicators, fluorescing compound and acrylic paint. To illustrate the curing mechanism, FTIR was performed on the modified paint during the curing processes in air at RT.

3.2.2. EIS characterization of acrylic-based coating

EIS experiments were conducted for acrylic-phenolphthalein coatings applied on AA 2024-T3. Indicator content in the acrylic paint was 0.5wt% and 2.4 wt %, with coating thickness of approximately 15 or 30 μm. Additional tests were performed for coatings containing 2.4wt% phenolphthalein and top-coated with 10 μm of pure acrylic.
Two or three samples were repeated for each case. EIS tests were performed after a range of prolonged immersion times, including the time for initial color change of the corrosion sensing coating. The EIS experimental parameters were as follows: 1 M NaCl, frequency range 0.01 to 10000Hz, 10pts per decade, and 10mv potential amplitude relative to the open circuit potential using an SCE electrode. The initial color change time was monitored during the immersion.

3.3. RESULTS AND DISCUSSION

3.3.1. Structure analysis results from FTIR

The characteristic FTIR peaks for acrylic without modification are shown in Figure 3.1. For uncured acrylic, the broad peak at 2710-3100 cm$^{-1}$ can be assigned to the CH group, while the peaks at 1710 cm$^{-1}$, 1600 cm$^{-1}$ and 3400 cm$^{-1}$ can be assigned to CO, CC double bond and OH stretching, respectively [104]. Some characteristic changes have been observed after curing (168 min in air at RT) of the acrylic paint. The broad peak area at 2700 - 3100 cm$^{-1}$ shrunk to a sharp peak at 2950 cm$^{-1}$, which could be associated with evaporation of solvent containing CH functional groups. The peak associated with the CC double bond at 1600 cm$^{-1}$ almost disappeared after 168 min curing, which can be attributed to polymerization processes during curing. All of these observations are correlated to the structure of acrylic before and after curing, as shown in Figure 3.2. The CO double bond is preserved during polymerization, while the CC double bond opens following the curing (or polymerization) process.
Figure 3.1. FTIR spectrum of acrylic paint at 0 and following 168 min of curing in air at RT.
Figure 3.2. The structure and polymerization process for acrylic and pH indicators and fluorescing compound used in this study. (a) Structures of acrylic before and after polymerization process; (b) Molecular structures of indicators (phenolphthalein and bromothymol blue) and fluorescing compound (7-hydroxycoumarin).
Different spectra are found for the modified acrylic paint containing color change pH indicators or a fluorescing compound. The area of the peak at 3400 cm\(^{-1}\) increased significantly with increasing phenolphthalein content in acrylic (from 0.1 to 2.4 wt %), as is shown in Figures 3.3 and 3.4. However, there is no observable change of peak area at 3400 cm\(^{-1}\) for acrylic paint containing 7-hydroxycoumarin or bromothymol blue, Figures 3.5 and 3.6. Other peaks associated with characteristic functional groups for acrylic, such as 1710 cm\(^{-1}\), and 1600 cm\(^{-1}\) did not change in intensity and exhibited no peak shift. The increase of peak area at 3400 cm\(^{-1}\) for the acrylic paint containing phenolphthalein at concentrations equal to or above 0.5 wt% may be explained by the hydrogen bonding or a secondary bonding between the acrylic and phenolphthalein due to an OH group contributed from phenolphthalein, Figure 3.2 (c). The negligible change of the peak at 3400 cm\(^{-1}\) upon addition of 0.1 wt% phenolphthalein may be due to the limited sensitivity of FTIR. The steric hindrance and stable structure possibly result in the less-noticeable band change at 3400 cm\(^{-1}\) for acrylic paint modified by bromothymol blue and 7-hydroxycoumarin.

The peak at 1710 cm\(^{-1}\) is assigned to the γ-CO stretching of acrylic and phenolphthalein, which is a characteristic bond for both acrylic and phenolphthalein, Figure 3.2 (a, b). Since there is no obvious shift in this peak with increasing phenolphthalein concentration as shown in Figure 3.3, 3.5, and 3.6, it can be concluded that no chemical reaction occurred upon mixture of acrylic paint with indicator compounds.

FTIR spectra for the various coatings during curing processes are shown in Figures 3.1 and 3.7-3.9. There is no peak shift for the characteristic absorption bands
mentioned above for the acrylic coating, but the peak shape and area differed with curing time. The spectra in Figures 3.1, 3.7 and 3.9 show that the truncated peaks at 2710-3100 cm\(^{-1}\) were reduced to complete peaks at 2950 cm\(^{-1}\) with a small shoulder at 2860 cm\(^{-1}\). The FTIR spectra for paint containing bromothymol blue, Figure 3.8, exhibited initial tri-peaks around 3000 cm\(^{-1}\) immediately following coating application on KBr. This may be due to a fast curing process for this paint that is not fully understood at this point. Following solvent evaporation from the paint, large amounts of functional groups containing CH would be removed from solution, which contributes to the significant decrease of peak intensity at 2710-3100 cm\(^{-1}\). The FTIR absorption band at 2720 cm\(^{-1}\) for all four paint/coating systems studied disappeared after short curing times (about 17 min), which is possibly also due to solvent evaporation. The peak at 1600 cm\(^{-1}\) disappeared after curing for pure acrylic and acrylic containing bromothymol blue and 7-hydroxycoumarin, Figure 3.1, 3.8, and 3.9, which is due to the opening of the CC double bond during polymerization processes, as is illustrated in Figure 3.2 (a). However, for phenolphthalein-containing acrylic coating, no significant peak decrease at 1600 cm\(^{-1}\) was found after as long as 4 months curing in air at room temperature, Figure 3.7. This may be a result of unfinished polymerization processes. For acrylic paint containing phenolphthalein, there is essentially no change of peak area at 3400 cm\(^{-1}\) during curing, Figure 3.7. This trend is more clearly demonstrated in Figure 3.10 after normalizing the peak area at 3400 cm\(^{-1}\) by the peak at 1700 cm\(^{-1}\), which is assigned to the CO double bond, which is a stable bond having constant peak area value during curing or polymerization.
Figure 3.3. FTIR spectrum of acrylic modified with phenolphthalein at content of 0.1, 0.5 and 2.4 wt%, and the spectra for unmodified acrylic paint and pure phenolphthalein were marked with 0 and 100 wt% respectively.
Figure 3.4. The effect of phenolphthalein content in modified acrylic paint on the normalized peak area at 3400 cm$^{-1}$ vs peak area of 1710 cm$^{-1}$. 
Figure 3.5. FTIR spectrum of acrylic modified with bromothymol blue at content of 0.1, 0.5 and 2.4 wt%, and the spectra for unmodified acrylic paint and pure bromothymol blue were marked with 0 and 100 wt% respectively.
Figure 3.6. FTIR spectrum of acrylic modified with 7-hydroxycoumarin at content of 0.1, 0.5 and 1.0 wt%, and the spectra for unmodified acrylic paint and pure 7-hydroxycoumarin were marked with 0 and 100 wt% respectively.
Figure 3.7. FTIR spectrum of acrylic modified with phenolphthalein 2.4wt% at the time of 0, 16, 32, 210 min, and 4 months during curing process in air at RT.
Figure 3.8. FTIR spectrum of acrylic modified with bromothymol blue 2.4wt% at the time of 0, 18, 35, and 210 min during curing processes in air at RT.
Figure 3.9. FTIR spectrum of acrylic modified with 7-hydroxycoumarin 1.0wt% at the time of 0, 17, 31, and 210 min during curing processes in air at RT.
Figure 3.10. The effect of curing time on the normalized peak area at 3400 cm\(^{-1}\) by peak area of 1710 cm\(^{-1}\). It illustrates practically no change of normalized peak area with prolonged curing time.
It can be concluded that the increase with phenolphthalein content of peak area at 3400 cm\(^{-1}\) associated with the OH group (Figure 3.4) is not due to the solvent content in the paint, but results from hydroxyl groups contributed from the phenolphthalein addition.

3.3.2 EIS results

Some of the EIS results on acrylic-based coatings were already reported in chapter 2. More EIS data and analysis will be presented here. Coatings that exhibited short times for initial color change had low pore percentage, \(S/S^0\), which is based on the breakpoint frequency, and high values of low frequency impedance, \(Z_{lf}\). This showed that the time for color change was controlled by the sensitivity of the coating to pH increase, and not by the coating protectiveness.

The other parameters that can be extracted from the EIS analysis can also be used to evaluate the coating protectiveness. Figure 3.11 shows the charge transfer resistance of various coatings measured at the time of initial color change. Like the low frequency impedance, the charge transfer resistance, \(R_{ct}\), was lower for coatings that exhibited higher times for initial color change. The pore resistance, \(R_{po}\), was also lower for coatings with higher times for initial color change, Figure 3.12. The fact that \(Z_{lf}\), \(R_{ct}\), and \(R_{po}\) were all lower for coatings with longer initial color change times indicates that the color change was not controlled by the protectiveness of the coatings. Instead, the sensitivity of the coating to pH was the controlling influence, as was discussed in Chapter 2.
Figure 3.11. Charge transfer resistance of different acrylic-phenolphthalein systems measured at the time of initial color change as a function of the time for initial color change.
Figure 3.12. Pore resistance of different acrylic-phenolphthalein coating systems measured at the time of initial color change as a function of the time for initial color change.
Figure 3.13. The relationship between the calculated value of water uptake based on the Brasher equation and immersion time in 1 M NaCl for acrylic coating modified with phenolphthalein at 0, 0.5, and 2.4 wt%. The data points are shown in three different kinds of markers and the trend lines are drawn from the logarithmic fitting.
Figure 3.14. The re-plot of data from Figure 3.13 in the fashion of normalized value of water uptake vs. time ($t^{1/2}/d$). The linear part of the fitting is by least square fitting and the horizontal line is by the average method.
To confirm that color change was not induced by an enhancement of the cathodic reaction due to the applied AC signal around $E_{oc}$ with a potential amplitude of 10mV during the EIS experiment, controlled samples were monitored with the same coating but without applied alternating potential/current. The results showed that the initial color change times were the same as those during the EIS test.

The EIS results provided more information than just coating resistance. The coating capacitance is related to the exposed area $A$, coating thickness $d$ and dielectric constant of the coating $\varepsilon$ according to:

$$C_c = \varepsilon \varepsilon_0 A/d \quad (3-1)$$

where $\varepsilon_0 = 8.85 \times 10^{-12}$ F/m is the electric permittivity of free space. Water uptake changes the dielectric constant of the polymer and therefore the total capacitance of the coating. The change of $C_c$ with time has been used extensively to study the water content of coatings on metal surfaces [40]. Water content, $\Phi$, determined from the following equation, known as Brasher's equation, has correlated well with gravimetric measurements [34,40]:

$$\Phi = (\log C_t/C_0)/ \log 80 \quad (3-2)$$

where $C_t$ is the capacitance at time $t$ and $C_0$ is the capacitance at time $t = 0$, 80 is the dielectric constant of water at 25°C. Figure 3.13 shows the relationship between the
water uptake from the Brasher equation and immersion time in 1 M NaCl for acrylic coating containing phenolphthalein at 0, 0.5, and 2.4 wt%. The rate of water absorption is seen to decrease with time. The smaller amount of water uptake for the coating with 0.5 wt% phenolphthalein compared to that for pure acrylic could be due to the hydrogen bonding between phenolphthalein and acrylic polymer matrix, which was shown in the FTIR spectra, Figure 3.3. The higher water uptake for the coating with 2.4 wt% phenolphthalein may be a result of precipitation of the pH indicator from polymer solution or residual acrylic monomer due to high phenolphthalein content as shown in Figure 3.7, which could increase the water uptake.

Using Fick's first law of diffusion with the boundary condition of a semi-infinite film exposed to an infinite bath of penetrant, the amount of water uptake has been related to diffusion coefficient by [113]:

$$\frac{M_t}{M_\infty} = \frac{4}{d} \sqrt{\frac{Dt}{\pi}}$$  \hspace{1cm} (3-3)

where $d$ is the coating thickness, $t$ is the time, and $M_t/M_\infty$ is the ratio of water uptake at time $t$ and infinity. The diffusion coefficient ($D$) was calculated from the slope of the linear relation between normalized value of water uptake vs. $t^{1/2}/d$ shown in Figure 3.14. The $D$ calculated from this method, $3.0 \times 10^{-9}$ cm$^2$ s$^{-1}$, is similar to a value reported for water diffusion in acrylic as determined by a gravimetric technique [113].
3.4. CONCLUSIONS

1. From the FTIR analysis, there is no structural change associated with the characteristic peak shift for the acrylic paint before and after modification by phenolphthalein, bromothylmol blue, or 7-hydroxycoumarin. The addition of pH indicators or fluorescing compound did not produce an observable peak shift associated with a chemical reaction between the polymer paint and any of the pH indicators.

2. Curing or polymerization processes for the modified acrylic paint did not appear to induce significant structure changes. The mixture may consist of indicator in solution with the polymer.

3. The sensitivity of corrosion sensing coating developed can be indirectly correlated to the electrical parameter of coating such as $R_{po}$, $R_{ct}$, and pore percentage calculated from the breakpoint frequency from EIS results. The acrylic-phenolphthalein coating system the coating with low pore coverage ($S/S_0$) had higher pore resistance $R_c$ and double layer resistance $R_{dl}$ at time of initial color change during immersion into 1M NaCl. The short immersion time for initial color change was associated with high sensitivity for corrosion detection.

4. Other analytical techniques and thermal analysis methods could provide further information. Nuclear Magnetic Resonance (NMR) should be done to confirm the structure information of modified acrylic paint/coating from FTIR spectra since more accurate and quantitative structure information can be resulted. Also Differential
Scanning Calorimeter (DSC) analysis might indicate polymerization (curing) processes for the different paint systems studied.
CHAPTER 4

SENSING LOCALIZED CORROSION OF AA 2024-T3 WITH MODIFIED AGAR-GEL

ABSTRACT

A new corrosion detection method, which uses modified agar-gel as a corrosion sensing medium, is introduced. Color-change or fluorescing compounds that are sensitive to pH were added to the agar gel in order to sense the pH change associated with the cathodic reaction that accompanies corrosion. The formation and structure of the modified agar-gel are discussed. Corrosion sensing behavior associated with the time for initial color change or fluorescing was demonstrated to be dependent on gel composition, corrosion initiation conditions, and surface conditions before applying the gel coating.
4.1 INTRODUCTION

The early detection of corrosion in aging aircraft has both economic and safety implications. In airplanes, corrosion may occur in relatively inaccessible locations, such as within the lap joints of the skin of an airplane. As a result, detection of localized corrosion in a large, complex structure such as an airplane is extremely difficult. Many different sensors and techniques are being developed to detect corrosion. However, these sensors are only effective if they are either physically located at the place where the corrosion is happening, or sensitive to corrosion occurring remotely.

As stated in an early chapter, a corrosion sensor should access the whole surface of a large structure such as an airplane in order to function effectively. Paint and coatings have such access. For localized corrosion such as pitting, crevice, and exfoliation corrosion, the cathodic reaction will tend to occur at locations nearer to the source of the cathodic reactant, i.e. oxygen in the air, compared to the anodic reaction. The oxygen reduction reaction will cause an increase in the local pH at the location where it occurs, so a coating that is sensitive to pH increases generated by the cathodic reaction will indirectly be sensing corrosion occurring nearby. It has been illustrated above that a polymer coating modified with pH indicators, such as phenolphthalein and bromothymol blue, or a fluorescing compound such as 7-hydroxycoumarin, can be used to sense the pH increase associated with the cathodic reaction of the corrosion process. The sensitivity in
terms of equivalent pit depth has been demonstrated to be about 10 \( \mu \text{m} \) for modified polymer coating systems.

Another approach to sensing corrosion is to use a temporary coating that would be applied for a short period in order to indicate where corrosion is occurring, and then removed. It is possible that the polymer coating might be stripped off during a regular maintenance inspection of an airplane, which could provide access to the underlying metal for a temporary coating. Agar gel is a good choice at this point due to its availability and solubility in water, which allows it to be easily removed\([114]\).

Agar has been used as an indicator carrier in various applications such as biochemistry\([115-117]\), medicine\([118]\), microelectronic sensors\([119,120]\), and corrosion\([121]\). Novotny et al.\([120]\) developed a thin electrode system with agar gel electrolyte as a support for the construction of bilayer lipid membranes that are stable to mechanical and electrical shock. Christensen et al.\([122]\) have applied chromogen agar paper (CAP) impregnated by an enzyme substrate and electron acceptor to diagnose diseases by the sign of color change induced by reaction during incubation. In the narrative of the motion picture “Corrosion in Action”\([123]\), agar was used as a vehicle for corrosion monitoring in several different experiments. An iron nail partially plated with Cu was immersed agar-gel that contained 1.2% agar, 3% NaCl, 1% phenolphthalein and 5% \( \text{K}_3\text{Fe(CN)}_6 \). This experiment clearly demonstrated the locations of the anodic and cathodic processes. The area around the dissolving iron was enriched in \( \text{Fe}^{2+} \) and reacted with \( \text{K}_3\text{Fe(CN)}_6 \) in which Fe is in the \( \text{Fe}^{3+} \) state to turn the gel blue. Near the copper side of the nail, the phenolphthalein turned red because of high concentrations of \( \text{OH}^- \) from the cathodic reduction reaction. Others used agar-gel as a medium to detect the corrosion.
processes of butt-welded panel and characterized the effect of surface pre-treatment on these regions by determining the anodic and cathodic regions[121].

The specific carrier capacities of agar-gel can be attributed to its chemical structure and physical properties. Agar is composed of gel-forming polysaccharides isolated from red sea-weed and has a linear polymer structure based on a disaccharide repeat unit that consists of alternating 3-linked β-D-galactopyranosyl and 4-linked 3,6-anhydro-α-L-galactopyranosyl units substituted with high levels of methyl ether groups [114], as illustrated in Figure 4.1. The relationship between gelling properties and agar-gel structure has been studied in detail [114,124,125]. Falshaw et al. reported a comparative study of the isolation, chemical structure, and gelling properties of nine agar species[124]. They found that methylation can significantly increase the gel-forming ability and the extent and position of methylation will affect the gelling/melting temperature of the agar gels, which correlated to the results from the previous study by Takano et al.[114]. Recently, Lai et al. researched the rheological and thermal characteristics of gel structures and showed that gelling (T_{gel}) and melting (T_{m}) temperatures, storage moduli (G') and the enthalpy (ΔH) values of agar gels were mainly associated with the viscosity of agar-gel[125]. Furthermore, they concluded that the rheological and thermal properties of agar-gel varied not only with the agar concentration, but also with the stage of the gelation process[125].

In this paper, an approach for corrosion detection using agar-gel as a carrier was studied. The agar-containing-solution was impregnated with a color-change pH indicator (or fluorescing compound) and NaCl at various compositions. NaCl was applied here with the consideration that the environment of the previously corroded area should be
reproduced in order for the modified agar-gel to detect its location quickly. Corrosion sensing behavior was studied by applying the modified agar-gel coating on AA2024-T3 after prolonged immersion time in 1M NaCl for corrosion initiation. The difference of pH sensing behavior associated with corrosion processes is discussed in relation to the gelation processes and the structure of modified agar-gels.
Figure 4.1. Structures of (1) idealised agar and (2) agar precursor with common positions of methyl ether substitution [12]
4.2 EXPERIMENTAL

4.2.1 Agar-gel Preparation and Characterization

Agar-gels were synthesized by the hydrolysis of polysaccharides with distilled water [124]. The procedure for modified agar-gel formation included three steps. Initially, agar powder was mixed with distilled water, NaCl and indicator chemicals (phenolphthalein or 7 hydroxycoumarin) in various amounts, as shown in Table 4.1, and the mixture was stirred using a magnetic stirrer for at least 1 h. The suspension was then heated to 80 - 95 °C and kept at this temperature for about 10-20 min before cooling. The beakers containing the suspension were covered by a glass cover to prevent or slow water evaporation during the heating processes. Finally, heating was terminated and the solution cooled to room temperature as stirring continued. The pH of the modified agar-gel solution was measured both before heating and following cooling.
<table>
<thead>
<tr>
<th>Gel component</th>
<th>Corrosion sample condition</th>
<th>Color change behavior</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Immersion time in 1 M NaCl</td>
<td>DI water washing</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Agar wt%</td>
<td>0</td>
<td>N</td>
</tr>
<tr>
<td>0.49</td>
<td>5 min</td>
<td>N</td>
</tr>
<tr>
<td>10 min</td>
<td>N</td>
<td>10 s</td>
</tr>
<tr>
<td>10 min</td>
<td>Y</td>
<td>54 s</td>
</tr>
<tr>
<td>30 min</td>
<td>N</td>
<td>10 s</td>
</tr>
<tr>
<td>30 min</td>
<td>Y</td>
<td>63 s</td>
</tr>
<tr>
<td>0.49</td>
<td>0</td>
<td>No change</td>
</tr>
<tr>
<td>5 min</td>
<td>N</td>
<td>38 s</td>
</tr>
<tr>
<td>5 min</td>
<td>Y</td>
<td>No change</td>
</tr>
<tr>
<td>10 min</td>
<td>N</td>
<td>18 s</td>
</tr>
<tr>
<td>10 min</td>
<td>Y</td>
<td>8 mins</td>
</tr>
<tr>
<td>30 min</td>
<td>N</td>
<td>20 s</td>
</tr>
<tr>
<td>30 min</td>
<td>Y</td>
<td>10 mins</td>
</tr>
<tr>
<td>132 min</td>
<td>Y</td>
<td>38 s</td>
</tr>
<tr>
<td>0.49</td>
<td>0</td>
<td>No change</td>
</tr>
<tr>
<td>5 min</td>
<td>N</td>
<td>15 min</td>
</tr>
<tr>
<td>5 min</td>
<td>Y</td>
<td>No change</td>
</tr>
<tr>
<td>10 min</td>
<td>N</td>
<td>120 s</td>
</tr>
<tr>
<td>10 min</td>
<td>Y</td>
<td>132 s</td>
</tr>
<tr>
<td>30 min</td>
<td>N</td>
<td>60 s</td>
</tr>
<tr>
<td>30 min</td>
<td>Y</td>
<td>80 s</td>
</tr>
<tr>
<td>0.49</td>
<td>0</td>
<td>No change</td>
</tr>
<tr>
<td>5 min</td>
<td>N</td>
<td>15 min</td>
</tr>
<tr>
<td>5 min</td>
<td>Y</td>
<td>No change</td>
</tr>
<tr>
<td>10 min</td>
<td>N</td>
<td>420 s</td>
</tr>
<tr>
<td>10 min</td>
<td>Y</td>
<td>12 min</td>
</tr>
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<td>30 min</td>
<td>N</td>
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</tr>
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<td>30 min</td>
<td>Y</td>
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<td>0.73</td>
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</tr>
<tr>
<td>10 min</td>
<td>N</td>
<td>10 s</td>
</tr>
<tr>
<td>20 min</td>
<td>N</td>
<td>33 s</td>
</tr>
<tr>
<td>0.24</td>
<td>0</td>
<td>No change</td>
</tr>
<tr>
<td>0 min</td>
<td>N</td>
<td>1 s</td>
</tr>
<tr>
<td>5 min</td>
<td>Y</td>
<td>1 s</td>
</tr>
<tr>
<td>0.24</td>
<td>0.01</td>
<td>1.7</td>
</tr>
</tbody>
</table>

Table 4.1. Corrosion sensing gel components and testing results
The critical pH value of color change or fluorescing behavior for modified agar-gel (with pH indicators or fluorescing compound) before and after the gelling process was measured by a titration test. NaOH (0.01M) was added into the stirred agar solution and agar-gel while the pH was monitored. The critical pH value was determined when the initial color change or fluorescing behavior under UV light source (MVP Inc, major beam wavelength 365 nm) was observed on the gel surface.

4.2.2 X-ray Diffraction Analysis

A Scintag Pad-V X-ray diffractometer (XRD) was used for X-ray diffraction examination of modified agar gel. The samples A1, B, and C listed in Table 4.2 were tested by XRD. The angle was scanned at 1 degree/min over a range of 25 - 60 degrees. The gel was spread on a plastic sample holder that was then placed onto the diffractometer. The software program Eva was used for analysis of the diffraction data by comparison with standard peak 2-theta values for pure chemicals such as phenolphthalein and NaCl.

<table>
<thead>
<tr>
<th>Sample No</th>
<th>Components</th>
<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Agar (g)</td>
<td>Pheno. (g)</td>
<td>NaCl (g)</td>
<td>H2O (ml)</td>
</tr>
<tr>
<td>Sample A1</td>
<td>0.2</td>
<td>0.02</td>
<td>0.7</td>
<td>40</td>
</tr>
<tr>
<td>Sample A2</td>
<td>0.2</td>
<td>0.1</td>
<td>0.7</td>
<td>40</td>
</tr>
<tr>
<td>Sample B</td>
<td>0.2</td>
<td>0</td>
<td>0</td>
<td>40</td>
</tr>
<tr>
<td>Sample C</td>
<td>0.2</td>
<td>0.1</td>
<td>0</td>
<td>40</td>
</tr>
</tbody>
</table>

*Table 4.2. Sample condition for XRD and ESEM analysis*
4.2.3 Sample Preparation

AA2024-T3 samples were cut into approximately 0.8 cm x 0.6 cm pieces and mounted in epoxy. The mounted sample surface was polished to 600 grit in water. Before testing, samples were stored in a desiccator for at least 24 hours to keep consistent surface conditions. Corrosion was initiated either by simple immersion in 1M NaCl solution or by applying an anodic current of 100 μA for 1 - 5 min.

The samples were then taken out of solution, rinsed with deionized water and dried with hot air, or just dried with hot air without water-washing, depending on the experimental conditions, Table 4.1. Finally, the gel coating was applied by dipping the pre-immersed samples into the gel suspension and slowly pulling them out. The time for initial color change was recorded from the moment of gel coating application. The properties of gel coatings were observed, such as the transparency of the coating, gel quality, and the coating aging behavior for different gel compositions.

4.2.4 ESEM Observation

In order to observe the morphology of gel coating after the gelation process, a Philips Environmental Scanning Electron Microscopy (XL30 FEG ESEM) was used at the condition of low vacuum since the gels contained a small amount of water. The chamber pressure was controlled at 4.9 torr of air. The agar-gel did not need to be electrically connected to the sample holder since the surface charging due to low conductivity, as in the situation of SEM, is minimized in the ESEM. Samples A2, B and C listed in Table 4.2 were examined by ESEM.
4.3 RESULTS AND DISCUSSION

4.3.1 Modified Gel Structure

In order to understand the physical and chemical interaction between the agar-gel and pH indicator (phenolphthalein), the structure and morphology of the modified gels will be presented first through the results of XRD and ESEM observations. Of the three gels examined by XRD, Table 4.2, only sample A1, which contained NaCl, exhibited strong diffraction peaks. The peaks were identified as being associated with NaCl. The absence of peaks associated with phenolphthalein is apparently the result of phenolphthalein being in the amorphous instead of the crystalline state.

ESEM photographs are shown in Figures 4.2. For the pure agar gel, sample B, no distinct objects are visible and the surface morphology is blurred, Figure 4.2. Due to the fragileness of agar, a highly focused electron beam would damage the agar structure and higher magnifications could not be achieved. For the sample containing NaCl, A2, dendritic structures were clearly seen among the background of the amorphous agar, Figure 4.3. The crystallized dendrites were loosely connected and agar gel was still present even inside the dendrites. For sample A2, which contained phenolphthalein, small round particles were seen at high magnification to exist in the amorphous agar that was inside the crystallized NaCl dendrite, Figure 4.4. These small shaped features may be phenolphthalein precipitates that formed either during gelation processes as some water was consumed by the hydrolysis reaction or because of water evaporation out of the gel. Similar round features were found by AFM for acrylic polymer coating containing small phenolphthalein.
Figure 4.2. ESEM (XL30 ESEM FEG) image of agar-gel coating (pure agar without indicators and NaCl) after applying on glass slide for 4 hr. No distinct objects were observed.
Figure 4.3. ESEM image of sample A2 after 4 hr on a glass slide.
Figure 4.4 (a). ESEM image of sample A2 after 4 hr on a glass slide. (b). High magnification of a.
precipitate (about 0.5-2.0 μm in diameter). It is proposed that the agar gel containing NaCl and phenolphthalein consists of loosely connected NaCl dendrites distributed in the amorphous agar substrate, with small roundish-shaped phenolphthalein particles precipitated out of the gel solution uniformly distributed within the gel. The agar-gel matrix probably still contains a high or even saturated concentration of dissolved NaCl and phenolphthalein that is in equilibrium with the precipitated solid. Therefore, the gel is almost saturated with phenolphthalein and NaCl. Since the purpose of applying a gel on bare Al alloy surface is to detect a pH increases associated with the cathodic reactions accompanying corrosion, it is this aspect of the gels that is expected to provide corrosion detection capability.

4.3.2 Corrosion Sensing Behavior

Corrosion sensing properties were evaluated by the initial color change time after applying the modified agar-gel on a sample surface, similar to the procedure used for the acrylic coatings described in a previous chapter. For phenolphthalein modified agar-gel systems, the time for initial color change (TICC) is plotted vs. prior immersion time in 1M NaCl in Figures 4.5 - 4.8. Almost all samples rinsed with DI water after immersion in 1M NaCl showed much longer TICC compared to samples tested without water rinsing. The TICC decreased with increasing immersion time in 1M NaCl for gels without NaCl and for gels with NaCl at low phenolphthalein content (0.05wt%), as shown in Figures 4.5 - 4.7. For the agar-gel system with NaCl and high phenolphthalein content (0.24wt%), the TICC was almost independent of the time of prior immersion, as is shown in Figure 4.8. High phenolphthalein content (0.24wt%) gels exhibited very
short TICC, especially for unrinased samples. Similarly, the presence of NaCl in the modified gel decreased the TICC.

The gel containing 7-hydroxycoumarin exhibited much shorter times for initial fluorescing behavior than the TICC for agar-gel systems containing phenolphthalein, Table 4.1. Besides the short time for fluorescing for 7-hydroxycoumarin modified agar-gel systems, fluorescence was also observed for an as-polished sample. In contrast, no color change was observed for phenolphthalein modified agar-gel without pre-immersion of the sample in NaCl. The result from the titration test showed that the critical pH value for the modified agar solution and gel was the same and equal to the value for the pure indicator compounds. The corrosion detection sensitivity for polymer coatings containing pH indicators was shown to be primarily controlled by the pH sensing behavior, so the high sensitivity for corrosion detection by the gel system with 7-hydroxycoumarin was anticipated given its low critical pH. The fluorescence observed for gels containing 7-hydroxycoumarin on as-polished samples may be related to a small amount of corrosion that occurred during the polishing in water.

The relationship between color change and corrosion will be described to confirm that the approach used previously for polymer paint can be applied to agar-gel systems. Figures 4.9 - 4.13 demonstrate how the modified gel acts as a corrosion sensor. The surface of an as-polished AA2024-T3 sample is shown in Figure 4.9 (a), (b). The surface is unattacked, except for some small pits that form during water polishing, Figure 4.9 (b). The AA2024-T3 sample coated by a modified gel containing 0.49 wt% agar, 0.24 wt% phenolphthalein, and 1.7 wt% NaCl without prior immersion in 1M NaCl gave no sign of color change after 5 h, as shown in Figure 4.10. The dark spots are due to the
accumulation of agar-gel after drying. After the gel coating was rinsed off, the surface exhibited the same "unattacked" morphology that was seen prior to gel coating, i.e. only the presence of small pits, Figure 4.11. It is indeed very important that the metal structure is not corroded by the gel coating. After pre-immersing the sample in 1M NaCl solution for 14 min and then applying the modified agar-gel, distinct red color spots could be observed within 10 s. The red color was maintained for a long time (>10hr), even after the gel coating dried. The gel coating on this sample after 4 h of coating application is shown in Figure 4.12. The right side of the sample exhibits a uniformly distributed red color. Figures 4.13 shows the image of sample after the gel coating was rinsed off. The surface is clearly corroded compared to as-polished surface shown in Figure 4.9. There is a correlation between the color change location seen in Figure 4.12 and the corroded areas indicated in Figure 4.13 (a, b, c). The zone of heavy attack shown in Figures 4.13 (b) and (c) can be associated with the center of the red region in Figure 4.12.

Since the corrosion potential of the AA2024-T3 was far below the reversible potential of oxygen reduction and hydrogen evolution, cathodic reactions associated with corrosion will result in pH increases that can in turn induce cathodic corrosion. So the region of color change might be associated with the location of cathodic dissolution for a sample surface previously immersed in NaCl solution.
Figure 4.5. The relationship of color change time of gel coating (0.49wt% agar, 0.24wt% phenolphthalein) and immersion time in 1 M NaCl for AA 2024 T3.
Figure 4.6. The relationship of color change time of gel coating (0.49wt% agar, 0.05wt% phenolphthalein) and immersion time in 1 M NaCl for AA 2024 T3.
Figure 4.7. The relationship of color change time of gel coating (0.49wt% agar, 0.05wt% phenolphthalein, 1.7wt% NaCl) and immersion time in 1 M NaCl for AA2024-T3.
Figure 4.8. The relationship of color change time of gel coating (0.49wt% agar, 0.24wt% phenolphthalein, 1.7wt% NaCl) and immersion time in 1 M NaCl for AA2024-T3.
Figure 4.9. AA 2024-T3 surface as polished to 600 grit in water, (a) and (b) have different magnification.
Figure 4.10. Modified agar-gel (agar 0.49wt%, phenolphthalein 0.24wt%, NaCl 1.7wt%) on AA 2024-T3 surface as polished to 600 grit in water without immersion in 1M NaCl, after 5hr (a) and (b) have different magnification.
Figure 4.11. AA 2024-T3 surface after coated by modified agar-gel (agar 0.49wt%, phenolphthalein 0.24wt%, NaCl 1.7wt%), for 5 hr and without immersion in 1M NaCl, (a) and (b) have different magnification.
Figure 4.12. Color change of modified agar-gel coating (agar 0.49wt%, phenolphthalein 0.24wt%, NaCl 1.7wt%) after applied on AA2024-T3 for 4 hr.
Figure 4.13. The AA2024-T3 sample surface after washing off the modified agar-gel coating that was the same composition as in Figure 4 and have been applied on AA 2024-T3 for 10 hr. There is some correlation between the location of color change (Figure 12) and the trench due to corrosion, as shown in (b) between two white dash line.
To confirm that pH increases cause color changes in the agar-gel, TICC was measured after gel coatings (0.49 wt% agar and 24 wt% phenolphthalein) were applied on AA2024-T3 samples that had previously been cathodically galvanostated to various charge densities before application of the gel. The results, Figure 4.14, indicate that TICC decreases with increasing cathodic charge and is apparently not influenced by whether or not the samples were washed with water after the cathodic treatment. The increase of accumulated OH\textsuperscript{−} with increasing cathodic charge be the reason for the shorter detection time. This trend is similar to that shown in the results for prolonged immersion test using the same gel coating system, Figure 4.5. However, the small difference in TICC for samples with and without water washing after the cathodic treatment is different than the immersion experiments where water washing had a big effect, Figure 4.5. The color change of modified agar gel applied to corroded or cathodically-treated samples after rinsing is similar to observations reported by Alodan and Smyrl\cite{126}, \cite{127}. They exposed Al alloys to chloride solutions containing fluorescein, a strong fluorescing dye or compound, and monitored the fluorescence with a confocal laser scanning microscope. Fluorescence was detected at certain intermetallic particles even after water washing\cite{126,127}.

The influence of viscosity or mass transport properties of the modified gel on the corrosion sensing process must be considered. It was observed that the color change for modified agar with uncompleted gelling process (heated to 75°C for 15min) spread away from the corrosion site, even beyond the edge of the Al alloy sample onto the epoxy mount, Figure 4.15.
Figure 4.14. The relationship of TICC of modified agar-gel containing agar 0.49wt%, phenolphthalein 0.24wt% with applying cathodic charge before applying gel coating.
Figure 4.15. Color change of modified agar-gel coating (same composition as in Figure 4) after applied on AA 2024-T3 for 4 hr. The color change have been observed out of the Al surface extending to epoxy mounting materials, which would be due to the transport of alkaline form of phenolphthalein or just transport of OH⁻ out of the surface.
This may be attributed to the diffusion of the alkaline form of phenolphthalein with different structure than the neutral or acidic form. To confine the location of the color change strictly within the cathodic area, agar-gel with high viscosity and slow mass transport should be used. On the other hand, a certain amount of transport of hydrogen or chloride ion is necessary to accelerate the processes of corrosion in the previous corroded/anodic area and pH value increase in the previous cathodic area so as to improve the corrosion sensing ability of the gel coating. In reality, both of the above arguments need to be considered to optimize the overall properties of accuracy and sensitivity. The effect of gelling temperature and agar content on the gel properties will be discussed next.

4.3.3 Modified Gel and Gel Coating

Now that the corrosion or pH sensing behavior of modified agar-gel has been described, the optimal gel properties for maximum corrosion sensing ability should be considered. Four gels with different component contents were studied for this purpose, Table 4.1. The gels contained agar, NaCl, and phenolphthalein in the following compositions: 0.49 wt% agar, 0.24 wt% phenolphthalein, with or without 1.7 wt% NaCl, remainder water, and 0.49 wt% agar, 0.05 wt% phenolphthalein, with or without 1.7 wt% NaCl, remainder water. The agar content of 0.49 wt% was kept constant because of the gelling properties, which will be discussed below.

The effect of phenolphthalein content on the TICC can be explained by the fact that the pH sensing mechanism of the indicator in the modified agar-gel did not change after the gelling process. The functionality of indicator, e.g. phenolphthalein, in agar-gel
has been illustrated in previous works [121,123,128], and it was shown above to be able to detect the pH increase associated with the cathodic part of a corrosion reaction. Since the critical pH value for color change for the modified gel determined by titration was the same as that of pure phenolphthalein (about 10), it can be assumed that the phenolphthalein and agar were simply physically blended after gelling. ESEM observation of phenolphthalein particles precipitated out of gel provided additional information about this physical-blending phenomenon between indicator and agar-gel.

Gels with or without NaCl sense corrosion by reacting with the high pH on the surface generated during the prior exposure to NaCl solution. The response of chloride-containing gels is faster because they replicate the corrosive environment and stimulate further attack. However, chloride-containing gels do not cause color change without the prior exposure to chloride solution, so do not cause the attack, but rather stimulate the response.

Water washing of the sample surface after immersion in 1M NaCl changed the surface condition in a way that neutralized the increased pH value associated with the cathodic reaction. So the color change or pH sensing behavior of modified agar-gel will exhibit decreased intensity and prolonged response time for a washed sample surface. On the other hand, the TICC is not lower for prolonged immersion time in the case of NaCl-containing gel because the critical pH value of the modified agar-gel is readily achieved by the replication of previous corrosion environment. The lack of dependence of TICC on immersion time (Figures 4.7 and 4.8) is associated with the corrosion sensing limit (or the smallest amount of corrosion that was detectable) of this NaCl-containing gel system.
One of the limitations of this technique so far is that the localized corrosion cannot be initiated in an accurately controlled manner. For samples with corrosion initiated by applying anodic current 100 μA for 1-5 min, which is enough time to generate localized corrosion, color change is still uniformly observed across the surface. This is in contrast to the localized spots observed for modified polymer sensing coating.

The appearance of modified gel coating was observed to correlate with its color change property. Gels with high agar content (>3.3 wt%) could not form smooth, transparent coatings due to the large size of agar particles that formed in suspension. On the other hand, coatings with low agar content (<1.0 wt%) could form very smooth and transparent coatings so that the color change associated with pit was easily distinguished.

For phenolphthalein modified gel coating with 1.7 wt% NaCl and 3.3 wt% agar, the color spots on the gel coating disappeared within 2-4 hr. This can be attributed to the high agar content of the gel, which increases the rate of the drying process and the gelling and melting temperatures [125]. Gelling temperature ($T_{gel}$) is the temperature at which the gel networks initiate through formation of helices and junction zones during cooling while melting temperature ($T_{m}$) is the temperature related to the dissociation of highly cross-linked junction zones of the gel networks during heating [116,125].

The agar content of a gel has been found to affect its thermal stability and the gel formation processes. Suspensions with very low agar content (<0.1 wt%) did not form a gel even after prolonged heating (4hr) at 80 - 95°C. Gels with < 0.2wt% agar are unstable and even at room temperature will decompose to lose the gel properties after a week. Re-heating to 80-95 °C and then cooling will not produce a gel reformation if water is added or not. On the other hand, the high agar content gel (>0.49 wt%) does not
change even after 2 month exposed to air at RT and its pH sensing properties do not change either. The fact that color change due to corrosion has been demonstrated to be lasting for a relatively longer time (several days) in a controlled humid environment indicates the relationship between corrosion sensing behavior and modified agar-gel properties [128]. Figure 4.16 shows the dependence of $T_{gel}$ and $T_m$ on agar concentration [125]. $T_{gel}$ values of around 30 and 15°C are predicted for agar contents of 0.5 and 0.2 wt%, respectively. This corresponds well with our observations of gel stability.

Interestingly, after water-spraying a dried gel coating containing phenolphthalein and a high agar content, red spots reappeared at the locations where the color change originated. However, this phenomenon was not possible for low agar content gels (<0.5 wt%), because the fact that coating itself was washed off. It was also found that, during heating, the suspension containing phenolphthalein changed color to light red from the light yellow that is the color of agar mixture suspension. But the red color disappeared upon cooling and gel formation at the room temperature. The red color during heating may be due to hydrolysis during gel formation [124], but the subsequent neutralization process after cooling down to room temperature is unclear.

The pH value of agar suspension and agar gel was found to be between 6.5-7.0 before and after heating, which is consistent with the yellow color of the gel or suspension at room temperature. In fact, it was reported that, in the processes of isolation of polysaccharide from seaweed or during the alkali treatment of native agar, the
Figure 4.16. Concentration dependence of gelling ($T_{gel}$) (A) and melting $T_m$ (B) temperatures of agar gels $^{[132]}$. The five different data series refer to the different kind of agar in the agar-gel systems.
intermediate solution was buffered at pH 6.8 [124]. However, there is no clear explanation in the literature for a pH increase during gelling processes at high temperature (80-95°C). One possibility is that hydroxyl groups from the methylated position such as at G-6 or LA2 were substituted by various O-linked groups, thereby leaving the solution alkaline during the heating processes [124]. In any case, it suggests that the color change or fluorescing behavior of the modified gel coating upon application on a sample surface was not associated with the gel pH value, but rather was induced by the pH increase associated with cathodic corrosion processes. In order to verify this, all types of gel composition used in this work have been coated on a glass slide, and there is no color change or fluorescing behavior during 24 hr observation period, during which color changes already happen on corroded Al samples.

4.4 CONCLUSIONS

The gel formation process, gel structure, and the corrosion sensing behavior on AA2024-T3 was studied for a modified agar gel. The following conclusions can be drawn:

1. Gel can be formed by blending pH indicator (phenolphthalein) or fluorescing compound (7-hydroxycoumarin) and/or NaCl with agar under heating and cooling processes. The content of agar, gel-forming agent, is critical for modified gel to have good film forming ability and optical properties for corrosion detection.
2. The modified gel has been demonstrated to be sensitive to corrosion processes by color change or fluorescing behavior under UV radiation, and there are direct relationships between the location of the color change and the corroded area.

3. The effect of indicator content and NaCl presence has been explored for different gel systems with or without water rinsing after prolonged immersion period in 1M NaCl. High indicator content and the presence of NaCl reduce the initial color change time upon gel coating application. The effect of NaCl content was explained by the replication of Cl\(^-\) in the previous corrosive environment.

4. Structures of modified gel were examined by optical microscopy, XRD, and ESEM. Precipitation of indicator (phenolphthalein) out of gel solution after water evaporation may lead to the corrosion detection by sensing pH increase associated with cathodic processes.

5. Gel-based corrosion sensing promises to be an easy, non-destructive and economic technique.
CHAPTER 5

CHARACTERIZATION OF pH AND CORROSION SENSING

EPOXY-POLYAMIDE COATINGS

ABSTRACT

Several selected pH indicators or fluorescing compounds were incorporated into epoxy polyamide paint. Color change or fluorescing behavior was studied and is discussed in terms of the intrinsic pH value of two components of epoxy. The corrosion sensing behavior has been determined and the results were explained by the pH sensing properties of modified epoxy paint from titration experiments. Results showed that color change pH indicators could be used to modify the epoxy coating to sense the cathodic reaction as long as the overall pH value was adjusted to below the critical pH value of color change for pH indicators. The fluorescing interference from both the resin and hardener components made it difficult to use fluorescence compounds for corrosion detection. Corrosion sensing properties of modified EP coating after dilution have been shown to depend on the pH sensing behavior of modified coating systems. Indicator-
containing epoxy coatings formed with neutralization and dilution appear to be promising candidates as effective corrosion sensing primer coatings.

5.1 INTRODUCTION

Corrosion damage in aging aircraft is receiving increasing attention in both military and commercial fleets so that the early detection of corrosion in aging aircraft has both economic and safety implications. In airplanes, corrosion in relatively inaccessible locations such as deep within the lap joints of the skin of an airplane is difficult to detect. A variety of methods have been applied to corrosion detection. Most of these methods have been used for field corrosion detection in airplanes, and some results have been demonstrated to be promising. However, only limited areas are detected so that these sensors are only effective if they are physically located at the exact place where the corrosion is happening [78,80-82]. Detailed descriptions of these methods are reviewed elsewhere [81,82] and are beyond the scope of this paper.

The basic idea of a paint-sensor is to modify paint to make it detect corrosion in some way since paint covers, and thus has access to, the whole surface of a plane. It is possible to sense either the corrosion process directly[80,81,89,129] or the pH change associated with the cathodic reaction that accompanies the oxidative corrosion reaction. The main cathodic reaction for atmospheric corrosion is oxygen reduction. For localized corrosion such as pitting, crevice and exfoliation corrosion, this cathodic reaction will tend to occur at more-accessible locations than the anodic reaction, i.e. nearer to the
source of oxygen in the air. If this cathodic reaction is separated spatially from the anodic reaction, it will cause an increase in the local pH at the location where it occurs. Therefore, a paint that is sensitive to pH increases generated by the cathodic reaction will indirectly be sensing corrosion occurring nearby. The pH indicators with color change properties have been used to sense the corrosion and study the mechanism of corrosion in the well-known Evans water drop experiment [18]. Color-change pH indicators have also been incorporated into organic coatings as a tool for determining the pH gradients associated with filiform corrosion beads [30].

Some fluorescing compounds can also detect pH changes. Fluorescent dyes were applied to microelectronic test vehicles to detect pH changes associated with corrosion of Al or Au metallization under an applied bias in a humid environment [91]. Fluorescing and color-change dyes have also been applied to Al after corrosion in order to identify the locations of the hydrous aluminum oxide corrosion product [92]. More recently, Johnson and Agarwala incorporated into epoxy paint different chemicals that fluoresce upon oxidation or upon complexation with metal cations formed by the corrosion process [80,129]. The usefulness of fluorescence compounds as indicators of coating damage when incorporated, in their oxidized state, into a primer coating was demonstrated [80,129]. Discontinuities in the topcoat, which did not contain fluorescence compounds, could be revealed by the fluorescence of the underlying primer. Such discontinuities represent sites where the risk of corrosion initiation is greatest, or where the build-up of underlying voluminous corrosion products has led to coating degradation. For the latter case, it was shown that fluorescence could be induced by the complexing of aluminum
ions with morin [129]. Others have explored a number of selected Schiff-base compounds as potential fluorescence-based indicators for metal surface corrosion [130].

In this study, several selected pH indicators or fluorescing compounds were incorporated into epoxy polyamide (EP) paint. Color change or fluorescing behavior was studied and is discussed in terms of the intrinsic pH value of two components of epoxy. The corrosion sensing behavior has been determined and the results were explained by the pH sensing properties of modified epoxy paint from titration experiments.

5.2 EXPERIMENTAL

The epoxy polyamide paint was provided by Deft Co., and was composed of two parts: neat (unpigmented) resin (compound A) and hardener (compound B). The pH value for both compounds was measured by pH paper. The EP was modified by adding seven different pH indicators or fluorescence compounds at certain concentrations (0.1, 0.5 or 2.4 wt%) to the mixture of resin (A) and hardener (B) (40g component B-catalyst for every 100g component A resin). The color change or fluorescing behavior under UV light (having a major peak at 365 nm) before and after curing at 100°C was monitored. In some cases the epoxy paint was diluted by a xylene-alcohol mixture solvent (1:1 ratio) to 50 vol% before mixing with pH indicators or fluorescence compounds. The hardener content was adjusted in the range of 5% - 40 wt% while the coating curing temperature was controlled at either RT or 100°C. Acetic acid was added to some mixtures to reduce the pH.
The critical pH value for modified EP coatings was tested by titration experiments. The pH sensing EP coating was applied on glass slides, which were immersed into stirred deionized water. Drops of 0.01, 0.1 or 1 M NaOH solution were added while the pH value was monitored and the color or fluorescence behavior was observed. The time for initial color change or fluorescence under UV radiation was also measured for coatings immersed in solutions at the critical pH.

Sensitivity experiments were performed on diluted EP-based indicator coatings applied onto AA2024-T3 substrates. A range of constant cathodic current was impressed on the sample, and the time for color or fluorescence change was monitored. This method was reported in Chapter 2 for testing acrylic corrosion sensing coatings. The EP coatings used in this test were about 30 µm in thickness and contained phenolphthalein at 1.0, 2.4, or 5.0 wt%.

5.3 RESULTS AND DISCUSSION

5.3.1 Modified sensing epoxy paint/coating

Properties of the A and B components, as well as a mixture of the two, are shown in Table 5.1. The hardener is seen to be quite alkaline, which is expected since it is an amine. The epoxy polyamide resulting from the mixture of A and B is also alkaline as a result of residual hardener. This mixture takes the yellow color of the hardener, and both components, as well as the mixture are seen to fluoresce blue. Given the fluorescence of the epoxy components, it is unlikely that a sensing coating containing fluorescing
compounds will be viable, and the work on EP-based coatings was focussed on the addition of color-change pH indicators.

<table>
<thead>
<tr>
<th></th>
<th>Resin Component A</th>
<th>Hardener Component B</th>
<th>Epoxy-polyamide (A + 40 wt% B)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>pH</strong></td>
<td>7.5</td>
<td>9-11</td>
<td>9-11</td>
</tr>
<tr>
<td><strong>Color</strong></td>
<td>Colorless</td>
<td>Yellow</td>
<td>Yellow</td>
</tr>
<tr>
<td><strong>Fluorescence</strong></td>
<td>Blue</td>
<td>Blue</td>
<td>Blue</td>
</tr>
</tbody>
</table>

(under UV light)

Table 5.1. Properties of unpigmented epoxy-polyamide components

The behavior before and after curing of modified EP coatings containing different pH indicators or fluorescence compounds is summarized in Table 5.2. The behavior of the pure indicator compounds and their content in the epoxies are also given. When indicators with critical pH value less than 11 were added, the color and fluorescence behavior of the epoxy polyamide reflected the high pH form of the epoxy polyamide. The behavior of epoxies containing indicators with high critical pH that did not change to the high pH form upon mixing were further tested by applying drops of pH 14 NaOH solution. Epoxies containing tropaeolin O and indigo carmine changed to the high pH form under the pH 14 drop, but the epoxy containing alizarin yellow GG did not change. The color change for indigo carmine was difficult to distinguish because the dark blue
background associated with the low pH form masked the yellow color of the high pH spots. It was interesting that EP paint containing 0.1 or 0.5 wt% phenolphthalein or 0.5 wt% coumarin reverted back to the low pH behavior (yellow color or blue fluorescence) after 24 hr curing at 100°C. The high temperature curing should enhance the curing process and reduce the residual hardener content. However, after the 24 hr 100°C curing the epoxy containing phenolphthalein did not change to the red high pH color upon application of pH 14 NaOH drops; it was inactive relative to pH sensing. The time for color change during mixing of phenolphthalein into the epoxy was shorter for 2.4 wt% than for 0.5 wt% phenolphthalein (< 1 min compared to about 5 min). Among these indicators, the color change time during mixing for bromothymol blue was the shortest (immediately after adding) due to its low critical pH value (about 7.6).
<table>
<thead>
<tr>
<th>Indicators</th>
<th>Std pH range for pure compounds</th>
<th>Std color Change</th>
<th>Content (wt%)</th>
<th>Color upon mixing</th>
<th>Color change at pH 14</th>
<th>Color change after 100°C 24hr</th>
<th>Color change at pH 14</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenolphthalein</td>
<td>8.2-10</td>
<td>Colorless → red</td>
<td>2.4</td>
<td>red</td>
<td>No change</td>
<td>Red → yellow</td>
<td>No change</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.5</td>
<td>red</td>
<td></td>
<td>Red → yellow</td>
<td>No change</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.1</td>
<td>red</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thymolphthalein</td>
<td>9.3-10.5</td>
<td>Colorless → blue</td>
<td>0.5</td>
<td>blue</td>
<td></td>
<td></td>
<td>No change</td>
</tr>
<tr>
<td>Bromothymol Blue</td>
<td>6.0-7.6</td>
<td>yellow → blue</td>
<td>0.5</td>
<td>blue</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alizarin Yellow GG</td>
<td>10-12</td>
<td>yellow → lilac</td>
<td>0.1</td>
<td>yellow</td>
<td>No change</td>
<td>No change</td>
<td>No change</td>
</tr>
<tr>
<td>Tropaeolin O</td>
<td>11-13</td>
<td>yellow → orange</td>
<td>0.1</td>
<td>yellow</td>
<td>yellow → orange</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Indigo Carmine</td>
<td>11.6-14</td>
<td>Blue → yellow</td>
<td>0.1</td>
<td>blue</td>
<td>Blue → yellow</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coumarin (fluorescing)</td>
<td>9.5-10.5</td>
<td>Nonfluor. → Green (fluoresc.)</td>
<td>0.5</td>
<td>green (fluoresc.)</td>
<td>Green → Blue (fluoresc.)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 5.2. Color change or fluorescence behavior of modified epoxy-polyamide (EP)
The behavior of the epoxy upon addition of various pH indicators suggests that the pH value of EP corresponds to > 10.5 in aqueous solution, which is about what is measured with pH paper, Table 5.1.

In order to be able to measure a pH increase associated with a cathodic reaction, the modified epoxy should have the color or fluorescing characteristics of the low pH form, and be able to switch upon exposure to high pH. The data in Table 5.2 indicate that, of the examined mixtures, only the epoxies containing tropaeolin O or indigo carmine are suitable. Furthermore, based on the behavior of modified acrylic coating systems described in Chapter 2, the sensitivity of such coatings to corrosion should depend on their critical pH; the most sensitive coatings have the lowest critical pH. In order to use indicators with low critical pH, the epoxy itself must have a low pH.

One way to reduce the pH of the epoxy is by reducing the amount of residual hardener after curing. In an attempt to enhance the extent of curing and thereby decrease the residual hardener content and the intrinsic pH value, the A-B component mixture was diluted with xylene-alcohol (1:1 ratio) to 50 vol%. The relative amount of hardener in the A-B mixture was also reduced. The pH value of diluted epoxy mixtures did not change for hardener component contents as low as 5 wt%. These mixtures, with 0.1 wt% phenolphthalein, changed color to red (the high pH color) upon mixing and curing, but they took much longer to do so (1-3 days) compared to the epoxy with more hardener and no solvent dilution.

Dilution with solvent also has the effect of increasing the solubility of pH indicator or fluorescence compound; for phenolphthalein the solubility increases to 12-14wt%. A mixture of 40 wt% hardener, 50 vol% xylene/alcohol solvent, and saturated
phenolphthalein was tested. In order to decrease the pH of this mixture, a few drops of acetic acid were also added. Using pH paper, the pH was found to be about 10.5 after addition of the acetic acid. This mixture stayed yellow upon mixing and further curing at room temperature. A titration experiment found the critical pH value for the cured coating to be 13. This coating, made with solvent addition, containing high indicator content, and adjusted to low pH with acetic acid appears to be a potentially viable epoxy-based sensing system because it has a low pH and remains active with respect to the external pH.

5.3.2 Sensitivity testing

Constant current sensitivity tests were used to evaluate the neutralized coatings made with the addition of the xylene/alcohol solvent and applied onto AA2024-T3. For coatings made without solvent addition, it was not possible to perform this test because the impedance was so high even after 2 days immersion in solution that no current could be passed. A meaningful open circuit potential measurement was also not obtained because of the barrier nature of the epoxy coating. In contrast, it was possible to use the constant current sensitivity test on the samples made with solvent addition. These coatings were thinner (30 μm compared to 45-50μm). Furthermore, the solvent addition may have resulted in a coating that was more permeable to water, i.e. less of a barrier.

The results of constant current sensitivity tests made on coatings made with solvent addition, 40 wt% hardener, acetic acid neutralization and 1.0, 2.4 or 5.0 wt% phenolphthalein are shown in Figures 5.1 and 5.2. Typical data obtained in a constant current sensitivity test are shown in Figure 5.1, which gives the results for the coating
Figure 5.1. A typical plot of time for initial color change per color spot vs various applying constant cathodic current in log - log scale for EP-phenolphthalein 2.4 wt% coating. The marks are data points and the line is the linear fitting by forcing the slope to be -1, which will give the sensitivity of corrosion detection associated with detectable pit depth.
Figure 5.2. The dependence of the calculated pit depth on the phenolphthalein content in modified EP coating after dilution with xylene/alcohol.
Figure 5.3. The relationships between critical pH value from the titration test, time for color change in critical pH solution and phenolphthalein content in modified EP coating.
containing 2.4 wt\% phenolphthalein. The rationale for this test and the method for calculation of the equivalent detectable pit depth are described in a previous chapter. Figure 5.2 shows that the corrosion sensitivity increases (detectable pit depth decreases) as the phenolphthalein content in the coating increases. Corrosion sensing ability of modified acrylic coating systems with different pH indicators or fluorescing compound has been shown to depend on their pH sensing properties, and not the coating protectiveness. This may also be the case for EP sensing coating systems. Figure 5.3 indicates that the critical pH decreases slightly as the phenolphthalein content increases. However, the time for initial color change in a solution having a pH equal to the critical value decreases significantly as the phenolphthalein content increases. This suggests that the decrease in detectable pit size is a result of the pH sensing ability of the coating.

5.4 CONCLUSIONS

Preliminary results of modified epoxy polyamide paint demonstrated that color change pH indicators can be used to modify the epoxy coating to sense the cathodic reaction as long as the overall pH value was adjusted to below the critical pH value of color change for pH indicators. The fluorescing interference from both the resin and hardener components made it difficult to use fluorescence compounds for corrosion detection. Corrosion sensing properties of modified EP coating after dilution have been shown to depend on the pH sensing behavior of modified coating systems. Indicator-
containing epoxy coatings formed with neutralization and dilution appear to be promising candidates as effective corrosion sensing primer coatings.

The protectiveness with respect to corrosion resistance of coatings formed with neutralization and dilution should be studied by techniques such as electrochemical impedance spectroscopy. High end point pH value indicators such as alizarin yellow GG or tropaeolin O need further study for use in un-acidied epoxy polyamide.
CHAPTER 6

SUMMARY AND SUGGESTIONS FOR FUTURE WORK

6.1 INVESTIGATION SUMMARY

In this thesis work, a novel non-destructive approach has been developed for corrosion detection, which uses modified paint/coating or agar-gel systems as a corrosion sensor. Various pH indicators or fluorescing compounds were mixed with polymer paint systems such as acrylic and epoxy or agar-gel to sense the pH increases associated with cathodic reactions. The modified coating or gel systems have been analyzed by different electrochemical (DC, AC technique) and materials analysis (FTIR, X-ray, SEM, etc) methods. The results can be summarized as follows:

I. Developed paint/coating systems containing color-change indicators or fluorescing compound were found to be sensitive to corrosion by illustrating the location of pH increase associated with the cathodic reaction that accompanies corrosion. The viability of using modified paint systems to detect hidden crevice corrosion in the underlying metal was also studied.
The following conclusions can be made:

i. Color change or fluorescence associated with the pH increases caused by the cathodic reaction in the corrosion process was easily detected by the naked eye.

ii. The critical pH for color change or fluorescence changed when an indicating compound was mixed with an organic matrix.

iii. The sensitivity of these coating systems was determined by passing cathodic current and determining the charge at which a color change or fluorescence was detected. The quantitative analysis of corrosion sensitivity for different coatings was calculated and evaluated as the depth of an effective pit. Pit sizes on the order of 10 μm were found to be detectable with the coating systems studied.

iv. The sensitivity of the corrosion-sensing coatings developed cannot be directly correlated to parameter extracted from fits of EIS data to equivalent circuit, such as Rpo, Rct, and pore coverage calculated from the breakpoint frequency. The time of initial color change during immersion was associated with sensitivity for corrosion detection.

v. Tests of the critical pH value of the corrosion sensing coating systems indicated that their corrosion sensing ability was directly related to the pH sensing behavior of the paint.

vi. The analysis of structures and functional groups using FTIR for coating systems with or w/o modifications and curing suggested that no structural change occurred, as evidenced by the absence of obvious characteristic peak shifts for the acrylic paint after modification by phenolphthalein, bromothymol blue, and 7-hydroxycoumarin before and after curing. The addition of indicators or fluorescing
compound did not produce new peaks associated with the functional groups. Curing or polymerization processes for the modified acrylic paint did not induce significant structure changes. The mixture of indicator and polymer apparently resulted only in physical blending.

II. The gel formation process, gel structure, and the corrosion sensing behavior on AA2024-T3 was studied for a modified agar gel. Since the previous approach of applying constant cathodic current was not applicable for this water-soluble systems corrosion detection ability was evaluated by the time for initial color change or fluorescing behavior after the agar-gel application on a corroded sample.

The following conclusions can be drawn:

i. Gel can be formed by blending pH indicator (phenolphthalein) or fluorescing compound (7-hydroxycoumarin) and/or NaCl with agar using various heating and cooling processes. The content of agar, the gel-forming agent, is critical if the modified gel will have good film-forming ability and optical properties appropriate to corrosion detection.

ii. The modified gel was demonstrated to be sensitive to corrosion processes by color change or fluorescence behavior under UV radiation. Direct relationships have been demonstrated between the location of the color change and the corroded area.

iii. The effect of indicator content and NaCl presence has been explored for different gel systems with or without water rinsing after prolonged immersion period in 1M NaCl. High indicator content and the presence of NaCl reduce the time required for
the initial color change following the application of the gel coating application. The effect of NaCl content was explained by the replication of Cl\(^-\) in the previous corrosive environment.

iv. Structures of modified gel were examined by optical microscopy, XRD, and ESEM. Precipitation of indicator (phenolphthalein) out of the gel solution following water evaporation may lead to the corrosion detection by sensing the pH increase associated with cathodic processes.

v. Gel-based corrosion sensors have the potential to provide an easy, non-destructive and economical means of sensing corrosion.

III. The results from modified epoxy polyamide paint demonstrated that color change pH indicators can be used to modify the epoxy coating to sense the cathodic reaction as long as the overall pH value was adjusted to below the critical pH value of color change for pH indicators. The fluorescing interference from both the resin and hardener components made it difficult to use fluorescence compounds for corrosion detection. Corrosion sensing properties of modified EP coating after neutralization and dilution have been shown to depend on the pH sensing behavior of modified coating systems. Indicator-containing epoxy coatings formed with neutralization and dilution appear to be promising candidates for effective corrosion sensors.
6.2 UNRESOLVED ISSUES AND SUGGESTIONS FOR FUTURE WORK

I. Modified acrylic coating systems:

1. pH indicators and fluorescence compounds, when added to the coating, have been shown to be qualitatively sensitive to corrosion. Quantitative estimates of the detectable amount of corrosion have also been made. However, determination of the total amount or type of corrosion associated with a given color change or fluorescence has not yet been achieved.

2. Color change or fluorescence behavior of modified acrylic coatings under various corrosion conditions have been investigated and promise to be a suitable approach for corrosion detection. However, in real situation, considering the examination time interval, the degradation of color change or fluorescence intensity with time should be calibrated to determine the time when corrosion occurred. This need to be further studied using acrylic coating systems, to provide fast correlation due to poor coating protection and controllable color change properties in terms of the different pH indicators or fluoresenting compounds applied.

3. Although the breakpoint frequency has been used as a high frequency parameter for fast evaluation of modified coating systems, the assumption of constant \( \rho \) and \( \varepsilon \) during the experiment is a controversial choice. Under certain conditions (e.g., long time immersion) in which \( \rho \) and \( \varepsilon \) are time-dependent parameters, how the analysis relates to coating behavior is an issue requiring further investigation.

4. The critical pH value for color change or fluorescence for the modified paint has been tested in the thesis work. But how it quantitatively relates to properties such as
sensitivity, initial time for color change or fluorescence behavior under immersion testing remains unknown.

5. Defects are known to be the common cause of coating failure and the location for cathodic reaction that constitutes the core part of our corrosion sensing approach. However, the relationship between defects in the coating and corrosion sensing behavior remains unknown.

6. It is generally accepted that pH redistribution under coating is the result of corrosion process. But the relationship among pH redistribution, corrosion under coatings and color change or fluorescing behavior of modified coating systems needs to be clear to quantify the corrosion detection ability.

II. Epoxy paint modification and corrosion sensing testing:

1. The usefulness of this approach with pigmented paints needs to be evaluated. The previous tested phenolphthalein and bromothymol blue pH indicator and 7-hydroxycoumarin fluorescing compounds need to be used for paint mixing. New indicators need to be tested for paint sensing properties. These will include Tropaeolin O, Indigo Carmine which has been shown to be promising based on previous results. Multiple pH indicator systems also need to be included to provide a larger pH detection range.

2. Neutralization of the hardener still needs to be studied for its influence on corrosion protectiveness. Different curing processes and coating composition (resin-hardener ratio) need to be studied by comparison of pH sensing behavior and corrosion protection through galvanistatic and EIS techniques.
3. The structure of modified polymer paint have been characterized for acrylic coating systems by FTIR; this suggested only physical or solution-type blending between the pH indicators or fluorescing compounds. The detail structure information of epoxy-polyamide paint after modification with various color change or fluorescing compounds is unclear. Analytical chemical techniques such as NMR, FTIR need to be used to study the epoxy coating chemical structure and direct the research of pH sensing behavior using anticipated chemical change after modification. Thermal analysis techniques, such as DSC, TGA, TMA should also be applied to evaluate the thermal behavior of modified polymer coating, such as Tg, Tm, and mechanical properties (modulus) further illustrate the thermo-mechanical behavior of corrosion sensing coatings.
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