

## **PH AND ELECTROCHEMICAL RESPONSIVE MATERIALS FOR CORROSION SMART COATING APPLICATIONS**

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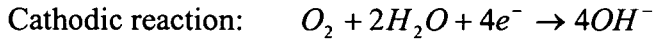
### **ABSTRACT**

Corrosion is a costly issue for military operations and civil industries. While most corrosion initiates from localized corrosion form, such as pitting, failure directly caused by localized corrosion is the most dangerous kind, because it is difficult to anticipate and prevent, occurs very suddenly and can be catastrophic. One way of preventing these failures is with a coating that can detect and heal localized corrosion. pH and other electrochemical changes are often associated with localized corrosion, so it is expected that materials that are pH or otherwise electrochemical responsive can be used to detect and control corrosion. This paper will review various pH and electrochemical responsive materials and their potential applications in corrosion smart coatings. Current research results in this field will also be reported.

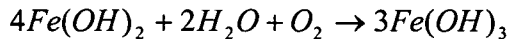
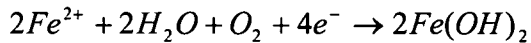
**Keywords:** smart coating, localized corrosion, corrosion sensing, corrosion inhibition, on-demand release

## INTRODUCTION

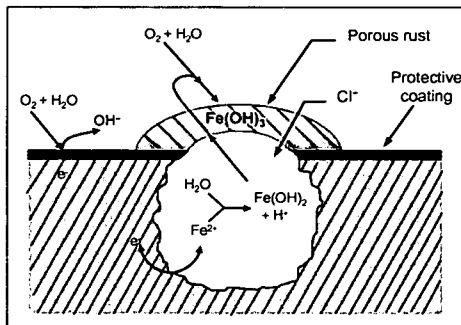
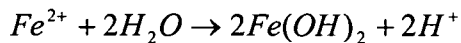
Corrosion is largely an electrochemical phenomenon, because, in most cases, it involves the transfer of electrons between a metal surface and an aqueous electrolyte solution. For instance, when iron corrodes in near neutral environments, the typical electrochemical reactions are:



In cases of localized corrosion, such as pitting corrosion, the anodic reaction happens in a small confined area, the metal ions produced are precipitated as solid corrosion products, such as  $Fe(OH)_2$  (often further oxidizes to  $Fe(OH)_3$ ), which covers the mouth of the pit (Figure 1. ).



This covering traps the solution in the pit and allows the buildup of  $H^+$ , through a hydrolysis reaction:



**Figure 1. The electrochemical cell set up between anodic and cathodic sites on an iron surface undergoing pitting corrosion.**

When chloride or other aggressive negative ions present, they diffuse into the pit to maintain charge neutrality. Consequently, the solution in the pit becomes highly acidic, lowering the pH. The overall effect is that, while localized corrosion happens, the anode area often has an acidic pH and the cathode area has an alkaline (higher) pH.<sup>1</sup>

Corrosion is a serious problem for most military operations and civil industries; the economic cost associated with corrosion is staggeringly high (about 3% of GDP). At least one third of corrosion failure are due to localized corrosion, such as pitting corrosion or stress corrosion cracking initiated by pitting. If localized corrosion happens without being detected, the failure can be disastrous. When human injury and life loss are involved, the corrosion cost is beyond measure. Thus, it is essential to detect localized corrosion at its early stage, and stop it when it is possible.

Various techniques have been developed to provide corrosion protection for metals, the most used approach is protective coating, which provide environmental barrier and sometimes additional protection by corrosion inhibitors. One of the new fields in coating research, stimulated by the need of replacing chromate coatings, is smart coating, which detects and/or healing corrosion at its early stage.

Because of the electrochemical nature of corrosion, it is expected that smart coating materials should be able to interact with the corrosion process (oxidation/reduction reactions), or corrosion products (such as metal ions or local pH conditions at cathodic or anodic sites, etc) and through that interaction, these materials provide corrosion indication or corrosion inhibition functions. In another word, it is expected to see some important materials for smart corrosion coating application should be pH sensitive or otherwise electrochemical responsive.

This paper will review various pH and electrochemical responsive materials and their potential applications in corrosion smart coatings. Current research results in this field will also be reported.

## PH INDICATOR AS CORROSION INDICATOR

### Visualizing Corrosion with the Aid of pH Indicator

pH indicators have been used for many years to determine the location and mechanisms of corrosion. For example, in the 1920s, Evans used indicators to locate the presence of anodic and cathodic sites during the corrosion of Fe.<sup>2,3</sup> In the 1950s, gels with indicators were used in an educational movie and its accompanying book, *Corrosion in Action*, to illustrate particular corrosion processes.<sup>4</sup> pH indicators were also added to paints to locate anodic and cathodic sites.<sup>5,6</sup> In a more recent study, a wide-range pH indicator was added to agar gel or to saturated sucrose solutions that then were used as media for studying the corrosion of Al to locate and observe the changes in pH at anodic and cathodic sites.<sup>7</sup>

Using a broad-range pH indicator, the corrosion of Al and Al alloys in chloride-containing agar gels was studied. Distinct changes in pH were observed at low-pH anodic sites and at high-pH cathodes. A good example can be seen in the following figures. Figure 2 shows the simple set up where, cells formed using chloride-containing agar gels. The gel was made up by adding 1 wt% of high-gel strength agar to the boiling salt solution. When the agar had dissolved, 15 vol% of the wide range pH indicator solution was added. The hot agar then was poured into a cell.

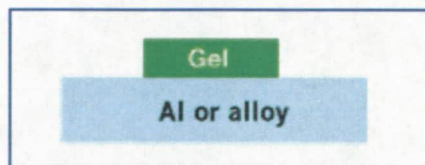


Figure 2. Cells formed using chloride-containing agar gels. (a) A simple cell placing agar directly on the Al surface.

Figure 3. shows the color correlation of the pH indicator, where Figure 4 shows color changes of the pH indicator associated with local corrosion sites.



pH	color
4.0	Red
5.0	Red-orange
5.5	Orange
6.0	Yellow-orange
6.5	Yellow-green
7.0	Dark greenish-yellow
7.5	Dark green
8.0	Light green
8.5	Bluish-green
9.0	Blue
9.5	Violet
10	Reddish-violet

Figure 3. Approximate correlation of pH with color using WRI and agar gel. The colors were taken from the gel and correlated with the pH and the colors described by the indicator manufacturer.

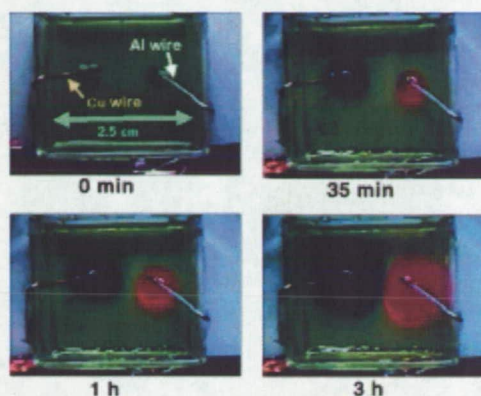
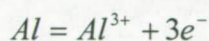


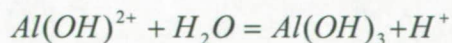
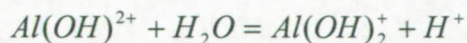
Figure 4. Increases with time in the size of regions where pH changes take place around Cu and Al wires forming a galvanic cell in agar containing 1 M NaCl.

The red coloration around the Al demonstrated that the pH had decreased to  $\leq 4$ . A pH of 4 was the lower limit of the indicator, but as diffusion was taking place, a gradient of hydrogen ion concentration above that indicated must have been present as the Al was approached. It also was concluded that the hydroxyl ion concentrations were greater than that for pH 10 because of the deep blue-violet color around the Cu electrode.

The reaction at the anode was considered to be:



followed by hydrolysis in stages as the pH increased. This is expressed in its simplest form as:



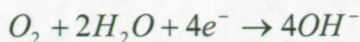
On connecting the wires, blue developed around the Cu and a smaller red disk appeared around the Al after the wires had been connected for 35 min and 1 h (Figure 6). Blue and red disks continued to spread, retaining their shape until they met after  $\sim 2$  h. The position of red and blue areas of contact then remained stationary as the colors continued to spread into the green areas, as seen after 3 h. A dark red arc also developed at the contact boundary of the acidic area and was attributed to the precipitation of



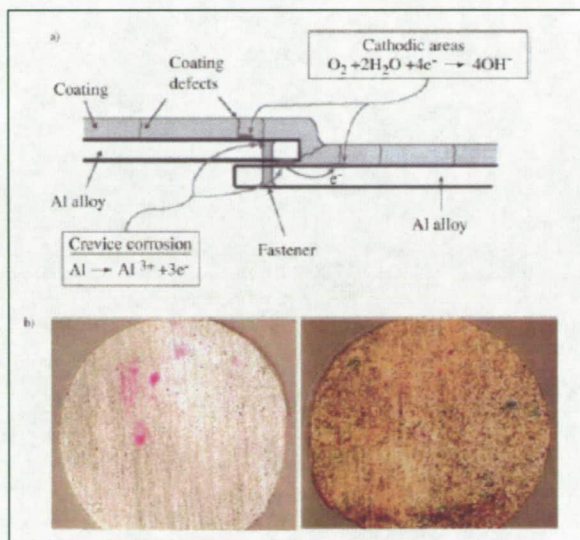
aluminum hydroxide,  $\text{Al}(\text{OH})_3$ , with the incorporation of the red indicator. This experiment was a clear demonstration that low pH values were associated with Al corrosion and the blue color with oxygen reduction at a cathode.

### Corrosion Indication Coating using pH Indicator

There are a variety of compounds that change color as a result of pH changes. Zhang and Frankel<sup>8</sup> used different color change or fluorescing compounds, which are sensitive to the increase in local pH associated with the cathodic reaction



accompanying the anodic reaction that forms hydrous aluminum oxide corrosion product. Figure 7 contains a schematic of an experimental painted lap joint setup for detecting crevice corrosion on aluminum panels (Figure 5a) and results on panels coated with acrylic paints containing pH indicators after immersion in 1 M NaCl solution for a period of time (Figure 1. b); color change in the coating indicated the occurrence of localized corrosion.



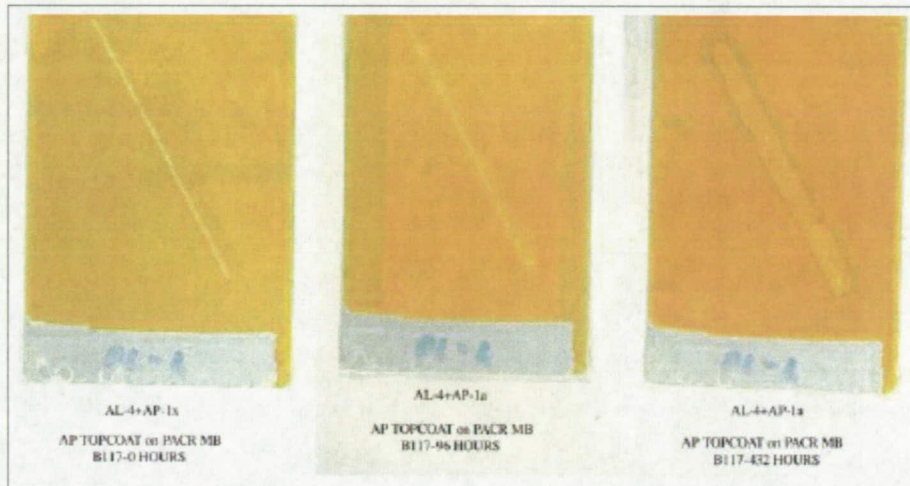
**Figure 5. (a) Experimental setup for determining crevice corrosion onset through color changes in painted lap joint. (b) Photographs of color change of two pH sensing coating on Al 5454 substrate following immersion in 1.0 M NaCl solution. Left: phenolphthalein paint after 8 days, Right: Bromothymol paint after 13 days.**

The use of cationic (e.g., montmorillonite) or anionic (e.g., hydrotalcite) nanoclays after exfoliation and planar orientation of the individual lamellae would also be expected to provide barrier properties. The presence of reactive sites on these clays could also offer the option of using them as carriers for pH responsive, color changing sensing additives such as ionizable dyes; such dyes have been used successfully for doping other inorganics such as mesostructured silica.<sup>9</sup>

The evaluation of nanoclays modified with pH sensitive colorants as sensors for onset of corrosion of polymer coated aluminum and ferrous substrates is part of a broad recent research program aiming at developing smart coating systems for military materiel with unique properties such as self-repair, selective removal, corrosion resistance, and sensing capabilities.<sup>10</sup> Preliminary data,<sup>11,12,13,14</sup>



indicate that it is possible to produce nanoclay based, well-dispersed, functional colorants for corrosion sensing and barrier improvement where the colorant is strongly bound to the clay, at concentrations as low as 1 wt% (based on clay). Furthermore, it is possible to detect development of localized alkalinity as a result of corrosion of metallic panels coated with acrylic, polyurethane, or epoxy paints through color changes as a function of time. Detection of onset of corrosion strongly depends on the initial color of the modified polymer paint. Figure 6 shows results of accelerated corrosion testing (ASTM B117) of aluminum panels coated with two paint layers. The bottom layer with poor protective capacity consists of a liquid acrylic coating containing a colorant modified nanoclay, whereas the top layer is a clear crosslinked acrylic powder with excellent protection characteristics. Development of blue color as a result of the increasing alkalinity accompanying corrosion at the scribed area is evident.



**Figure 6. Accelerated corrosion testing in salt fog spray chamber (two layer structures—tape protected exposed area) of scribed aluminum panels. From left to right: 0, 96, 432 h.**

## FLORESCENT COMPOUND AS CORROSION INDICATOR

### Fluorescence and Corrosion

Fluorescence is a luminescence that is mostly found as an optical phenomenon in cold bodies, in which the molecular absorption of a photon triggers the emission of another photon with a longer wavelength. Usually the absorbed photon is in the ultraviolet range, and the emitted light is in the visible range, but there are exceptions. Fluorescence is named after the mineral fluorite, composed of calcium fluoride, which often exhibits this phenomenon. Fluorescence can occur in minerals, in organic molecules, in lanthanides and actinides and in semiconductor and polymer nanoparticles.<sup>15</sup>



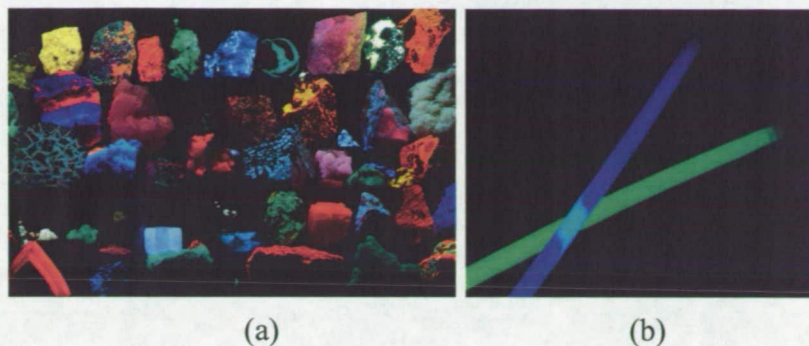


Figure 7. (a) Fluorescent minerals, and (b) green and blue glow sticks, which oxidize phenyl oxalate ester in order to produce light.

Fluorescent Compounds have been investigated for their corrosion-sensing capabilities when subjected to the effects of temperature, pH, reduction, and oxidation behavior. For corrosion sensing, the chemical compounds should show a change in fluoresce only when either oxidized or when reacting with the corrosion product, such as metal or  $H^+/OH^-$  ions, generated during corrosion.

From a practical standpoint it is easier to see small areas of fluorescence against a non-fluorescent background than to see slight decreases in overall fluorescence. In other words, it is preferable to have an increase in fluorescence as an indicator of corrosion. A wide range of chemical species are responsible for destroying fluorescence, a process known as quenching. Organic molecules which fluoresce tend to be planar, rigid and unsaturated, such as polycyclic aromatics. When such molecules have adjacent groups capable of coordinating to metal centers then they will form complexes. The formation of such a complex can result in chelation enhanced fluorescence (CHEF) or chelation enhanced quenching (CHEQ). Many CHEF probes have been developed for biological and other studies and are commercially available. Sibi and Zong<sup>16</sup> have demonstrated the use of such probes for the detection of aluminum corrosion under a paint film. An ideal probe has an excitation wavelength well removed from the emission wavelength, a high stability constant for the complex formed and a large CHEF effect. Compounds such as fluorescein, Morin or Schiff bases, oxines and hydroxyquinolines, were found to fluoresce has been test for corrosion indicators. While the simplest detection method would be a color change, such as using phenolphthalein to detect the alkalinity formed at cathodic sites, greater sensitivity can be achieved by using a fluorescent compound since the detection limits in solution for fluorescence are lower by factors of  $10^2$ – $10^4$  than for colorimetric light absorption.<sup>17</sup>

### Fluorescent Compounds Used as Corrosion Indicator

#### *8-hydroxyquinoline-5-sulfonic acid (8-HQS)*<sup>17</sup>

Bryant and Greenfield have developed a method for detecting under-film aluminum corrosion using a hand-held UV inspection lamp based on the chelation induced fluorescence of 8-hydroxyquinoline-5-sulfonic acid (structure shown in Figure 8).



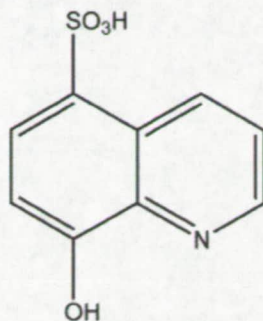


Figure 8. Structure of 8-hydroxyquinoline-5-sulfonic acid hydrate.

A solution in dimethyl sulfoxide was prepared by dissolving 8-HQS and polyvinyl alcohol. A thin film of this solution was deposited on a standard aluminum test panel using a draw-bar set at 100 microns gap. The solution was allowed to dry in air for 48 h and then further drying carried out at 60 °C in an oven. The aluminum surface had an even, yellow coloration. The surface was then coated with epoxy resin. The exposed edges were coated with beeswax and the film was scored with a scalpel and exposed to a salt spray. The plate is visualized using a hand-held UV lamp with a maximum output centered at 373 nm. Figure 9 shows an aluminum test panel where the salt induced corrosion can be clearly seen where the coating has been scored by a scalpel and where bubbles in the epoxy have allowed salt attack. The same study found that fluorescence is quenched by ferrous and ferric ions but this effect is minimal in the presence of excess fluoride ion. Epoxy resins transmit light in the near UV to a greater degree than polyesters or polyurethanes. Chloride ions pass through a polyurethane film more readily than aluminum or ferric ions.

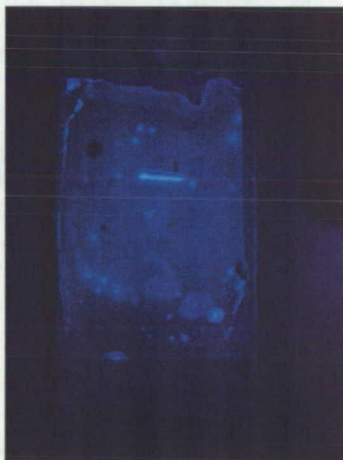


Figure 9. Coated aluminum test panel in UV light showing corrosion where the film is scored.

A compound with similar structure (shown below), 8-hydroxyquinoline (oxine) within coatings was used to detect corrosion on Al7075 plates.<sup>18</sup> Oxine forms a fluorescent complex with aluminum oxide and in several tests utilizing 7075 alloy plates; there was a significant difference in fluorescence intensity in the unprotected 7075 and the protected 7075ccc plate. This was also verified for plates painted with acrylic paint, clear polymer-adhesive film, epoxy paint, and even epoxy paint with the



oxine absorbed in silica. Oxine has proved to be a true corrosion detector for aluminum and its alloys. Figure 11 shows an example of the oxine in coating indicating corrosion process.

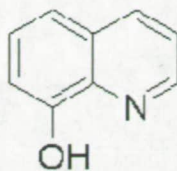


Figure 10. Oxine structure

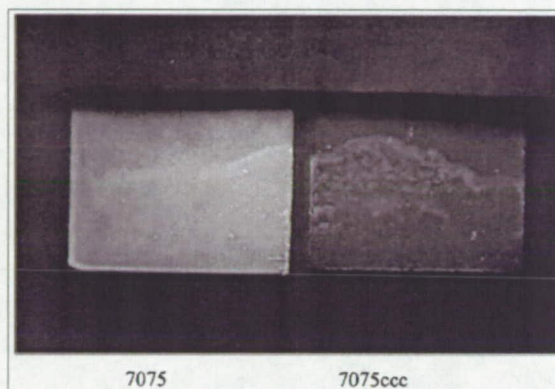


Figure 11. UV light photograph of oxine under acrylic paint on 7075 and 7075ccc aluminum alloy plates. Lighter areas show the fluorescence. After aging 39 months at room temperature.

### Phenylfluorone<sup>19</sup>

Li et al prepared a fluorescent sensing coating for monitoring corrosion of aluminum alloys by incorporating phenylfluorone (PF) (structure shown below) into acrylic paint as sensing material. The fluorescent dye PF reacts with aluminum ions on corroded aluminum substrate to occur fluorescence quenching observed in UV light. This paint system is sensitive to underlying corrosion processes through reacting with the  $Al^{3+}$  produced by anodic reaction. (Figure 13) After the samples of Al alloy 2024 coated with PF-acrylic paint were immersed in 1M NaCl solution, fluorescence quenching spots can be seen. With the development of corrosion process, the size of fluorescence quenching spots increases. Active corrosion areas on the sample surface were found under the fluorescence quenching spots by optical microscope. (Figure 14) SEM confirmed that the fluorescence quenching spots are the local corrosion sites. The sensitivity of this coating system was tested and it was found that pit with an approximate depth of 50  $\mu m$  can be observed through fluorescence change.

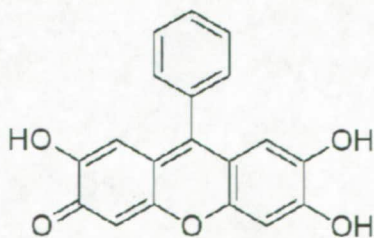


Figure 12. Structure of 9-Phenyl-3-fluorone

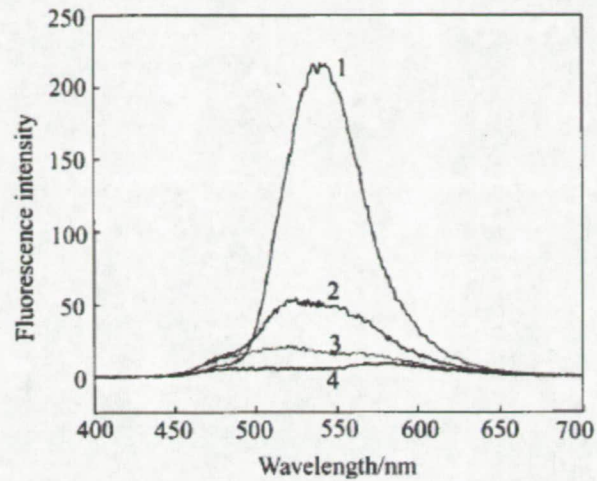


Figure 13. Fluorescence of PF without  $Al^{3+}$ (1) and with 10%  $Al^{3+}$ (2), 20%  $Al^{3+}$ (3) and 30%  $Al^{3+}$ (4).

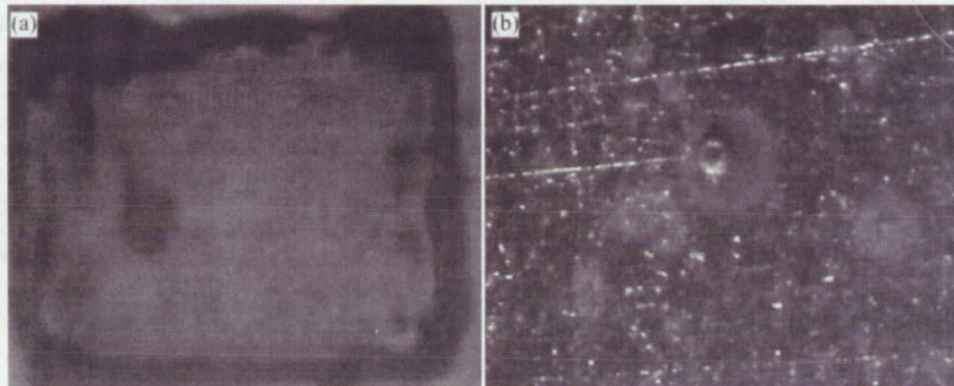


Figure 14. Photographs of fluorescence quenching under *UV* light (a) and metal surface under fluorescence quenching spots under optical microscope (b).

### *Lumogallion*<sup>16</sup>

Sibi and Zong described a method is described using fluorescence probes for determination of metal ions in corrosion processes of Al 2024T3. lumogallion (3-(2,4-dihydroxyphenylazo)-2-hydroxy-5-chlorobenzenesulphonic acid), *N,N'*-bis-(salicylidene)-2,3-diaminobenzofuran (SABF) and Phen Green™ were used to study their response to  $Al^{3+}$ ,  $Mg^{2+}$  and  $Cu^{2+}$ , respectively, in aqueous solution and corrosion processes. Their structures are shown below. Fluorescence intensity of lumogallion and SABF increased with increasing concentration of  $Al^{3+}$  and  $Mg^{2+}$ , respectively. The emission intensity of Phen Green™ was observed to decrease with increasing  $Cu^{2+}$  concentration. The variation in emission intensity is dependent on ion concentration and showed a linear relationship.



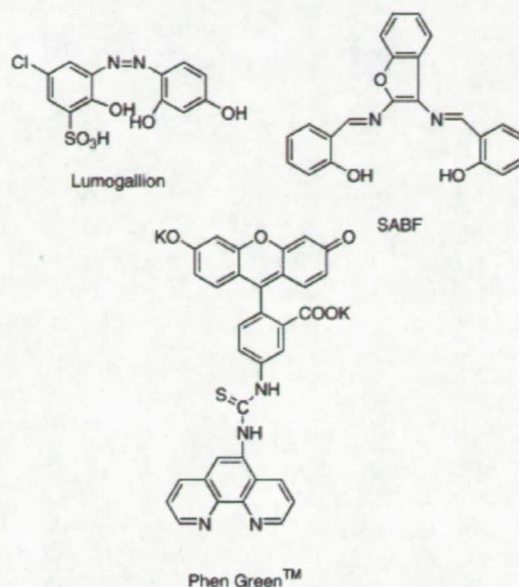


Figure 15. Chemical structures of fluorescent compounds.

The fluorescence emission intensity of 0.50 M NaCl corrosion solution increased with exposure time. Soluble  $\text{Al}^{3+}$  and  $\text{Mg}^{2+}$  can be determined in corrosion solution and  $\text{Al}^{3+}$  and  $\text{Mg}^{2+}$  reached 0.126 and 2.344  $\mu\text{M}$  in 1 week, respectively.  $\text{Cu}^{2+}$  cannot be detected in corrosion solution. The anodic dissolution of Al matrix and Al–Cu–Mg particles developed  $\text{Al}^{3+}$  and  $\text{Mg}^{2+}$ , but Cu was left at the metal surface.

Al 2024T3 panel was abraded with sand paper (600 mesh) to remove oxide surface, followed by washing with hexane to clean the surface. The applied epoxy/polyamide coating is typical for aircraft primers from Shell Chemicals. Lumogallion was dissolved into a mixture of xylene and acetone, and then added to epoxy/polyamide solution. After sufficient mixing, the resin solution was cast on panel 2024T3 by draw-down bar. The specimen was cured at room temperature for at least 2 weeks, and the coating thickness was approximately 20–40  $\mu\text{m}$ . The panels were sealed with Scotch Brand tape (3M Corp.), except for the exposure surface, and then were immersed in 0.50 M NaCl solution, the fluorescence images were observed on a fluorescence microscope after specified exposure time. Uniform emission background produced by excitation of fluorescent probes indicated that lumogallion was well-dispersed in the epoxy/polyamide primer. Visible fluorescence image changes revealed corrosion processes of Al 2024T3 under protective coatings. Energy dispersed X-ray (EDX) and scanning electron microscopy (SEM) were employed to confirm the results obtained. The fluorescence image and SEM image are shown in the following pictures.



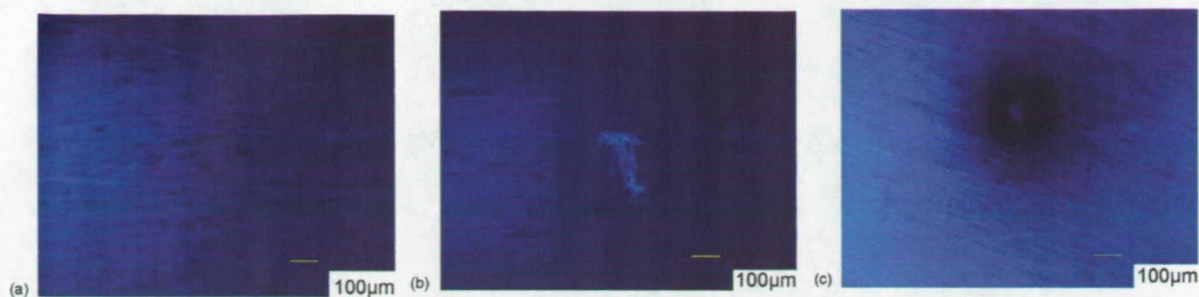


Figure 17. Fluorescence image of epoxy/polyamide primer with lumogallion: (a) initial surface; (b) 12 weeks exposure to 0.50 M NaCl solution; (c) 16 weeks exposure to 0.50 M solution.

### Summary

In the research field of fluorescence –based corrosion indicators, there are three major objectives: to screen, design, synthesize and characterize potential fluorescence-inducible compounds, (2) to determine the fluorescence characteristics under corrosion conditions of oxidation/reduction, metal chelation and pH's, and (3) to formulate in paint/primer system to develop 'smart' coatings for detecting hidden corrosion of substrate metal. The approaches that have been taken including: (1) screen known highly conjugated organic compounds, (2) synthesize new compounds such as Schiff-base of Salicylaldehyde with amine-substituted anthraquinones and benzophenones, (3) investigate fluorescence spectral characteristics under redox conditions and in the presence of selected surface coatings. (4) select promising candidates for exploring their sensor potential (5) Study the fluorescence properties in coatings for corrosion detection. A corrosion sensing coating concept is shown in Figure 16 that can incorporate various fluorescent compounds.

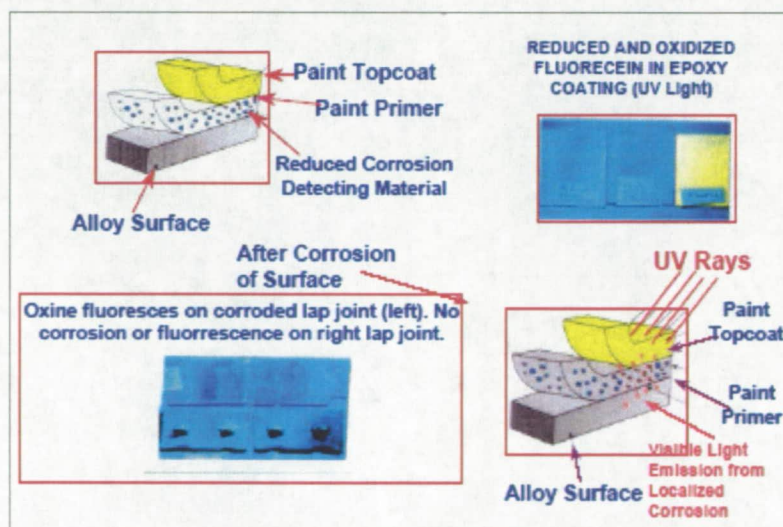


Figure 16. Fluorescent materials for corrosion detection on alloy surfaces.

The promising show significant fluorescence peak and/or shift, through corrosion related changes, either through some Redox changes, Chelation sensing, or pH sensing. The candidate compounds includes:

Fluorescein, Morin, Oxine, Calcofluor and Dayglo  
Schiff bases of



- (1) 2-aminoanthraquinone with salicylaldehyde (2AAQS)
- (2) 2,6-diaminoanthraquinone with salicylaldehyde (2,6DAAQS).

Although fluorescent compounds show great promise as corrosion indicators, there are some technical challenges associated with them, such as low solubility of Schiff bases in solvents, fluorescence changes to be enhanced, redox reactions do not occur in cured epoxy paint, redox reactions are not always reversible, and fluorescence quenching by coating constituents.

## **CORROSION INHIBITOR CONTROL RELEASE BASED ON PH SENSITIVE MATERIALS**

The best coatings for corrosion protection provide not only barriers to the environment, but also a controlled release of a corrosion inhibitor, as demanded by coating damage and the presence of a corrosive environment. It was assumed that one of the reasons that make Chromates the most effective corrosion inhibitors, besides being a very strong oxidizer, is their low solubility in water, and increased solubility under basic condition at cathodic site of localized corrosion.<sup>20</sup> Many effective corrosion inhibitors that were studied as chromate replacements share one common problem, high solubility in water. It prevents them to be used as paint pigments in paints, as they would cause blistering in the presence of moisture. Thus controlled release function is vitally important to develop corrosion inhibiting pigments in order to achieve paint compatibility. There is also the environmental concern. It is well known the reason that the ban of chromate is due to their toxic and carcinogenic nature. But nearly all powerful inhibitors may have detrimental effect on environment, when released in substantial amount. They would present an environmental problem if their release mechanism were simply leaching. Hence, better approaches, controlled release, must be pursued earnestly.

Different approaches have been used to develop a corrosion-responsive protective coating. For instance, Yang and van Ooij<sup>21</sup> have encapsulated soluble corrosion inhibitors using plasma polymerization to achieve a slow release of the inhibitor through diffusion process. While such approach lowers the solubility of inhibitors in water, it is based on a mass-action governed release mechanism, not a selective process for damage-induced activation.

A similar effect was achieved in sol-gel hybrid films developed as a replacement of chromate pre-treatment. Corrosion inhibitors were doped into oxide nanoparticles and the porous sol-gel network structures to achieve are used as reservoirs for corrosion inhibitors, for storage and prolonged release of inhibitors.<sup>22,23, 24</sup>

Another approach is to use ion exchange corrosion-inhibiting pigments. It has been considered for a number of years. The most recent work was that performed by Williams and McMurray, who demonstrated that hydrotalcite, rehydrated in the presence of inhibitor anions such as phosphate and chromate, provides excellent inhibition for filiform corrosion.<sup>25</sup> The ion exchange pigments, when formulated in paint, work to limit filiform corrosion in at least two ways: by lowering the chloride activity through ion exchange and by buffering the anodic head of the filiform.

While those above methods are improvements from simple leaching release, our interests are in the release mechanisms that are triggered by the electrochemical environment directly related to corrosion.

### **Conductive Polymer for corrosion protection**

Intrinsically conductive polymers (ICPs) were discovered in late 1970, for which Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa received the Nobel Prize in Chemistry 2000. Since their

discovery, they have been investigated for various applications in different field, due to their unexpected combination of properties: they behave like semiconductors, but can be easily processed like polymers.

ICPs are also, probably, the most studied smart materials for corrosion protection, yet their potential for this application is still a topic of current controversy. An updated discussion on this topic is provided by Rohwerder and Michalik.<sup>26</sup> Although the controversy cause frustration to the researchers in field, it is not entirely surprising. ICPs are not simple materials, their behave in a corrosion environment, which is complicated and constantly changing, should not expected to be straight-forward.

Since the fist reports<sup>27,28</sup> on corrosion protection by ICPs, many studies have been performed in order to understand the protection mechanisms. Although the nature of corrosion protection of ICPs have proven to be elusive thus far, useful insights have been provided as results of the studies. Some proposed that ICPs in their oxidized state may act as an oxidizer, as most anodic inhibitors, provide anodic protection through improving the oxide layer at the interface between polymer and metal, even keep metal passivated in the presence of small defect. Some suggest a cathodic protection theory; ICPs shift the reaction site of oxygen reduction from the metal/polymer interface into the polymer, which reduce the concentration of free radical  $\text{OH}\cdot$  at the interface, thus reducing the rate of cathodic reaction.

Amongst the proposed mechanism, the most interesting one is the "on demand" release of corrosion inhibiting anions. Barisci et al<sup>29</sup> pointed out that, under corrosion condition, ICPs could be reduced and release their dopants because of the galvanic potential difference between the metal and ICPs. ICPs can be potentially used for corrosion resistive coatings when corrosion-inhibiting compounds are chosen as dopants.

Kinlen et al<sup>30</sup> and Kendig et al<sup>31</sup> and showed that anion release in polyaniline (PANI) likely by the higher pH caused by the oxygen reduction reaction at cathodic sites.

Kinlen demonstrate that conductive PANI "passivates" pinhole defects in coatings on carbon steel using scanning reference electrode technique (SRET). PANI were doped with both sulfonic acid and phosphonic acid, using different polyaniline salts: (PANI-p-toluenesulfonic acid, PANI-dinonylnaphthalene disulfonic acid, and PANI-dinonylnaphthalene sulfonic acid, PANI-Aminotri(methylene phosphonic acid), PANI-methylphosphonic acid. Polyvinylbutyral (PVB) was used as base resin for PANI coating formulation. The PANI-PVB coatings were brush-applied on C1018 steel coupons. It is shown that phosphonic acid salts of PANI are more effective for corrosion protection than sulfonic acid salts, as phosphonic acid doped PANI coating shows significant anodic passivation whereas the sulfonic acid doped PANI does not. It was proposed that, for a scribed coating, PANI salt release the dopant anion and protons. Then  $\text{Fe}^{2+}$  reacts with dopant anion in an anodic regime where the insoluble iron-dopant salt formed to passivate the anodic area.

Kendig et al reported their results for inhibiting anion-doped conducting polymer coating on Al 2024. PANI-containing coating was doped with ORR (oxygen reduction reaction) inhibitors. When the coated Al 2024 was scribed and exposed to salt fog, the scribe area appeared to be protected, presumably by the released inhibitors. A more elaborated mechanism was proposed to explain the anion release process.

Paliwoda-Porebska<sup>32</sup> showed a potential driven inhibitor anion release in polypyrrole (Ppy) coating. In this study, water dispersion of Ppy doped with  $\text{MoO}_4^{2-}$  or  $[\text{PMo}_{12}\text{O}_{40}]^{3-}$  was mixed with a non-conducting polymer matrix polymer, and then the mixture was applied on iron sample by spin coating. The  $[\text{PMo}_{12}\text{O}_{40}]^{3-}$  doped Ppy coating showed a significant inhibition of delamination and a partial passivation of the defect, presumably through on demand release of inhibitor anions. The  $\text{MoO}_4^{2-}$  doped Ppy coating, on the other hand, show no inhibition effect on the delamination process. It is assumed that the alkaline pH at the delamination location caused over-oxidation, which hindered the release of  $\text{MoO}_4^{2-}$  ions.  $[\text{PMo}_{12}\text{O}_{40}]^{3-}$  doped Ppy was not affected, as an anion decomposition reaction took place which buffered the high pH at cathodic sites.



While these researches shed lights on our understanding on the corrosion resistance mechanism of conductive polymers, and showed that ICPs are promising candidate for corrosion inhibitor controlled release in coatings, they do not answer all the questions. Still others seek the explanation why ICPS seems to often provide corrosion protection in some cases, immersion condition and/or in the presence of small defects, while fail to do so in others, in the presence of big defects, or after long term of exposure to corrosive environment. Rohwerder et al<sup>26</sup> explained these observations in terms of a switch ion exchange mechanism during the reduction of ICPs, from mixed anion release and cation incorporation to an exclusive cation incorporation over extended length scale. While we believe that this proposed mechanism is at least partially correct, a better term can be used to paint a clear picture: potential gradient. When there is only a few small active defects in the coating, the potential gradient of the field is very high around the defects, high potential gradient, means higher current density, also higher release rate, in case of anion release. When there is bigger defects, or longer exposure time, i.e. more active defect sites, the electrochemical field changes, and the potential gradients are lower, meaning lower inhibitor anion release rate, resulting in less effective corrosion inhibition. A more detailed modeling of the electrochemical field in the presence of active defects will be provided later for a more elaborated explanation, based on the potential gradient concept.

### **Surface Modified Nanoparticles as Corrosion Inhibitors**

Nanoparticles have been used for carrier or reservoirs for active compounds, such as in drug delivery and catalyst applications, due to their high surface areas and potential for enhanced functions through surface modification. As mentioned above, sol-gel nanoparticles and other nature-engineered nanostructure, such as hydrotalcite, have been used for carriers of corrosion inhibitors, and some have been claimed to have active corrosion protection, such as Ce-modified hydrotalcite conversion coatings. However, a close study on their function shows that the inhibitor release is still through leaching, or diffusion due to simple concentration gradients or ion exchange process; the active corrosion protection is originated from none but the electrochemical and physical properties of the inhibitor.<sup>33</sup>

Cook at TDA Research proposed that nanoparticles can be surface modified so that corrosion inhibitors can be attached to the nanoparticle through a chemical bond; by choosing the chemical bond that would break under corrosion condition or in contact with corrosion product, the surface modified nanoparticles would function as corrosion resistant pigments that release corrosion inhibitor on demand.<sup>34</sup>

The core material of this technology is a common mineral, boehmite, white and relatively soft basic aluminum oxide [AlO(OH)], which is readily commercial available. The commercial form of boehmite can be easily converted into nanoparticles. It was found that the chemical bond between a carboxylate and the boehmite particles is cleavable by hydroxide ions. So that boehmite particles can serve as corrosion resistant pigments that release corrosion inhibitor on demand, when they are corrosion indicators are bonded to the boehmite surface through a carboxylate bonds.

To demonstrate this technique, acrylic acid was covalently bonded to the boehmite nanoparticle surface by heating them together in water; then the particles were heated in water with 2-amino-6-methylbenzothiazole, a well-known organic inhibitor for cathodic inhibition. After that, the particles were spray dried and the powder was added to the epoxy of a two-component epoxy primer. This nanoparticle inhibitor containing epoxy coating has shown excellent protection for high strength Al alloys.

## PH SENSITIVE MICROCAPSULE FOR CORROSION SENSING AND PROTECTION

We developed a controlled release system that combines the advantages of corrosion sensing and corrosion protection by using pH-triggered release microcapsules for early detection of corrosion and for corrosion protection.

This approach has all the advantages of a polymer microcapsule design. It is very versatile, can be used to encapsulate unlimited number of materials, in both solid and liquid phase, even gas phase entrapped in aerogel. After these microcapsules are formed, it is easy to incorporate them into composite or coatings. For corrosion application, various compounds, such as corrosion indicator, inhibitors, self healing agents, and dyes can be encapsulated. These microcapsules can be incorporated into various coating system for corrosion detection and protection (Figure 17). The versatility of the design is of special interest in corrosion inhibition application. Almost all corrosion inhibitors are chemically active reagents, and often the reactivity that makes them effective corrosion inhibitors also causes them to be environmentally unfriendly, such as chromate. Because of this, research for new and environmentally friendly corrosion inhibitor is an on-going effort in corrosion protection industry. After a new inhibitor is developed, it usually takes a long time to adopt the new inhibitors into a paint formula, by adjusting various factors in the paint formulation. The smart coating the including encapsulated inhibitor can avoid this long reformulation process for new inhibitors by simply changing the core content of the microcapsules.

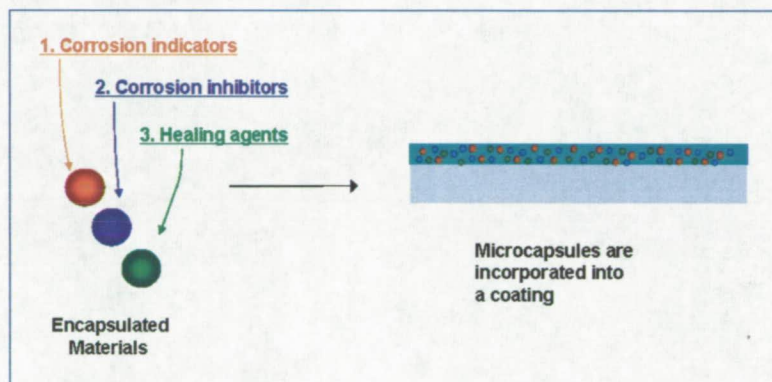


Figure 17. Smart coating with pH sensitive microcapsules for corrosion detection and protection.

While the pH microcapsule design has all the advantage of regular microcapsule design, it has one more advantage that others do not have. It has the true control release functions for corrosion application. Regular microcapsules release its contents when it is mechanically damage, these pH sensitive capsules release its contents when corrosion occurs. Mechanical damage in a coating is one of the important causes for corrosion of the base metals; however, it is not the only one. Many forms of defects in coating, such as air bubble, uneven thickness, or edge effect, will results in poor protection of the coating and cause corrosion to happen. The pH sensitive microcapsule will release its content for corrosion detection or protection whatever the cause is. This can be understood based on the electrochemical nature of corrosion and the release mechanism of these microcapsules.



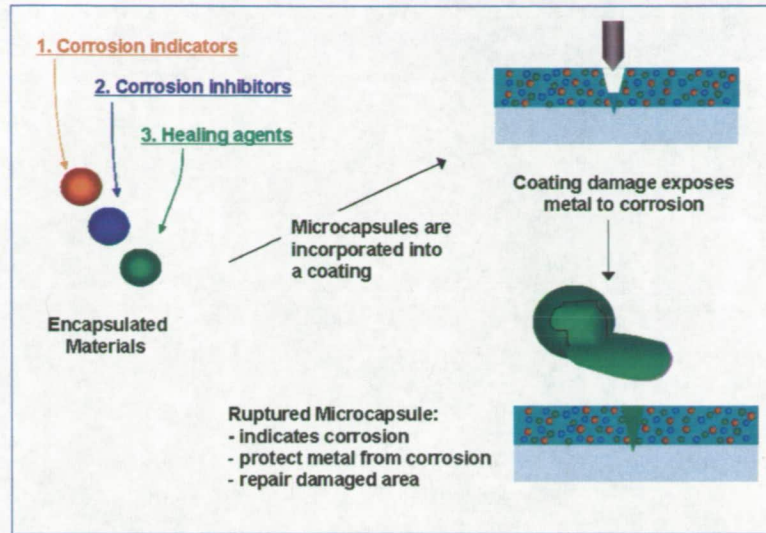


Figure 18. Smart coating with microcapsules release encapsulated materials when mechanically damaged.

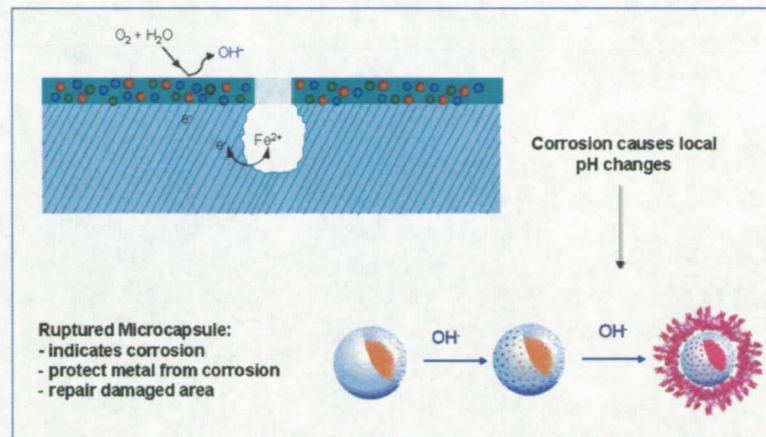


Figure 19. Smart coating with pH sensitive microcapsules release encapsulated materials when localized corrosion occurs.

The critical component of this new smart coating system is the pH-triggered release microcapsules. Their content can be completely released in a relatively short amount of time, such as four hours, when the environmental pH is around 8 - 10, or 1 - 4. These pH ranges match those present in localized corrosion conditions in near neutral environments. The pH sensitivity and controlled release function of these microcapsule is based on hydrolysis reaction of degradable polymer.

While controlled release microcapsules are a new application in the corrosion field, the controlled release concept is not new. Much can be learned from the biodegradable materials studies in controlled release in medical and agricultural applications, such as drug and pesticide controlled releases.

Most biodegradable materials break down through hydrolysis or enzymatic activity. There are four main types of hydrolysis-susceptible bonds. They are, in the order of increasing stability, anhydrides, esters, carbonates, and amides. Among these polymers, polyesters are relatively stable, with a half-life of 3.3 years for a hydrolysis rate without a catalyst,<sup>35</sup> but can undergo a rapid hydrolysis reaction when catalysts (under basic or acid conditions) are present. The microcapsule wall breaks down as a result of the ester hydrolysis reaction. These reactions can be catalyzed by acids and based

thus making the microcapsule pH-sensitive. While the acid catalyzed mechanism is the reverse of the Fischer esterification<sup>36</sup>, the base catalyzed mechanism is the most used route. Because of the strongly nucleophilic reagent, OH<sup>-</sup>, this reaction is essentially irreversible.

## SUMMARY

Corrosion is a costly issue for military operations and civil industries. While most corrosion initiates from localized corrosion form, such as pitting, failure directly caused by localized corrosion is the most dangerous kind, because it is difficult to anticipate and prevent, occurs very suddenly and can be catastrophic. One way of preventing these failures is with a coating that can detect and heal localized corrosion. pH and other electrochemical changes are often associated with localized corrosion, so it is expected that materials that are pH or otherwise electrochemical responsive can be used to detect and control corrosion. This paper will review various pH and electrochemical responsive materials and their potential applications in corrosion smart coatings. Current research results in this field will also be reported.

For corrosion sensing applications, both color and fluorescent pH indicators have been incorporated into coating system. Although there are still technical challenges associated with them, they are showing great promise for industrial application. If a low opacity coating system is used, then compounds which visibly change color may be employed. Corrosion reactions depend on the substrate and its pretreatment, but in those cases where corrosion produces ions which raise the pH, a simple indicator compound may be sufficient. In practice, fluorescent compounds are more readily detected by optical equipment than visible compounds. Several such materials including fluorescein, Schiff bases, oxines and hydroquinolines will change from inactive to fluorescent as a result of corrosion reactions. UV scanning equipment combined with instrumental measurement of the intensity of the emitted light allows the development of fluorescence to be quantified and the extent of corrosion mapped.

For inhibitor controlled release application, conductive polymers and surface modified nanoparticles were studied as potential materials. While conductive polymer's ability and mechanism for corrosion protection is still under debating among different research groups, it showed potential as for "on demand" release of corrosion inhibiting anions, at least in some studies. Nanoparticles, derived from a commercially available mineral, boehmite, have been used as inhibitor carrier, and their surfaces have been chemically modified, so that it would release the inhibitors when corrosion occurs.

pH-triggered release microcapsules have developed for smart corrosion application. These microcapsules are susceptible to the cathodic pH condition and can release their content when localized corrosion occurs. For corrosion application, various compounds, such as corrosion indicator, inhibitors, self healing agents, and dyes can be encapsulated. These microcapsules can then be incorporated into various coating system for corrosion detection and protection applications.



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