

## **Corrosion Sensing Smart Polymeric Coatings**

**Ajit Behera\*, S.C Mishra and P. Parida**

Department of Metallurgical & Materials Engineering  
National Institute of Technology, Rourkela-769008, Odisha, India

\*Corresponding Author, email id: ajit.behera88@gmail.com

### **Abstracts**

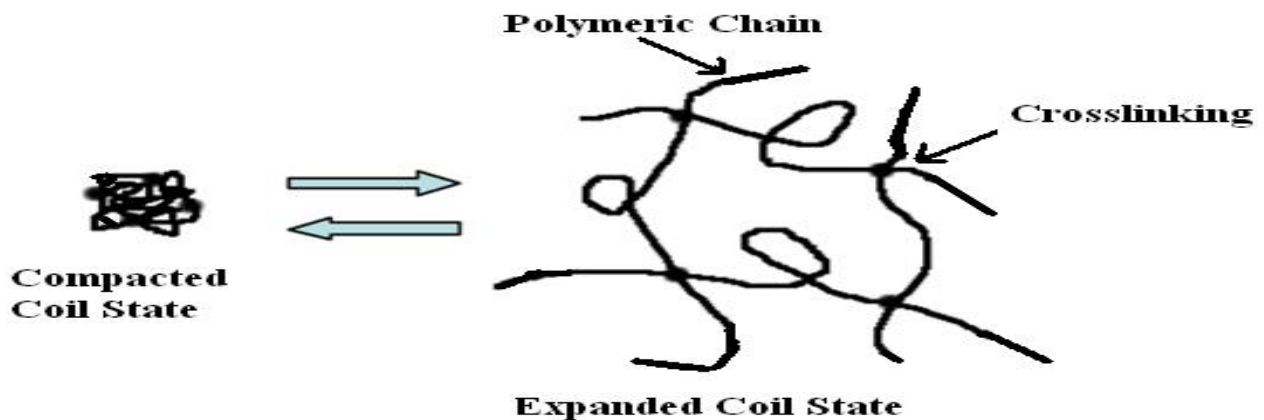
Smart materials cover a wide and developing range in engineering & medical application. This paper presents the “Stimuli-sensitive/smart” polymeric systems which can overcome dramatic property changes responding to small changes in its surrounding environment. Here there is a corrosion resistant or protective smart polymeric coating and paints have been described. Additional smart-coating principles potentially relevant to corrosion sensing that are clear from experimental view. The system includes the paint systems containing color-changing compounds, responding to  $p^H$  changes that results from corrosion processes. Changes of coating compounds from nonfluorescent to fluorescent states, upon oxidation or complexing with metal cations. Release of color dyes containing anticorrosive additives from embedded layer filled with dye and additive following mechanical damage of the coating. This experiment shows and identify the location of the hydrous aluminum oxide corrosion product by fluorescing and color-changing dyes which is applied to Al alloys. Smart polymers are becoming increasingly more prevalent as scientists learn about the chemistry and triggers that induce conformational changes in polymer structures and devise ways to take advantage and control them. New polymeric materials are being chemically formulated that sense specific environmental changes in biological systems, and adjust in a predictable manner making them useful tools for drug delivery or other metabolic control mechanisms.

Key words: Smart polymer; corrosion; Aluminum.

### **1. Introduction**

Materials that formally have the label of being smart include piezoelectric materials, electrostrictive materials, electrorheological materials, magnetorheological materials,

thermoreponsive materials, pH-sensitive materials, ultraviolet-(UV) sensitive materials, smart polymers, smart gels (hydrogels), smart catalysts, and shape memory alloys. Among these smart materials, polymeric Smart materials have been expanded to materials that receive, transmit, or process a stimulus and respond by producing a useful effect that may include a signal that the materials are acting upon it. Some of the stimuli that may act upon these materials are strain, stress, temperature, chemicals (including pH stimuli), electric field, magnetic field, hydrostatic pressure, different types of radiation, and other forms of stimuli [1]. The effect can be caused by an absorption of a proton, of a chemical reaction, of an integration of a series of events, of a translation or rotation of segments within the molecular structure, of a creation and motion of crystallographic defects or other localized conformations, of an alteration of localized stress and strain fields, and of others. The effects produced can be a color change, a change in index of refraction, a change in the distribution of stresses and strains, or a volume change [1]. The main properties of smart polymers are that they are strong, flexible, easy to colour, easy to mould, and tough [2]. Some uses of smart polymers are: Nappies [3], helmets [4], plastic bags [5], textile [6], non-stick chewing gum, plastic bottles etc. one example in smart polymer is the polymer-polymer and the polymer-solvent interactions (solvent that in biomedical applications will be usually water) show an abrupt re-adjustment in small ranges of pH or temperature, and this is translated to a chain transition between extended and compacted coil states (as shown in figure-1).

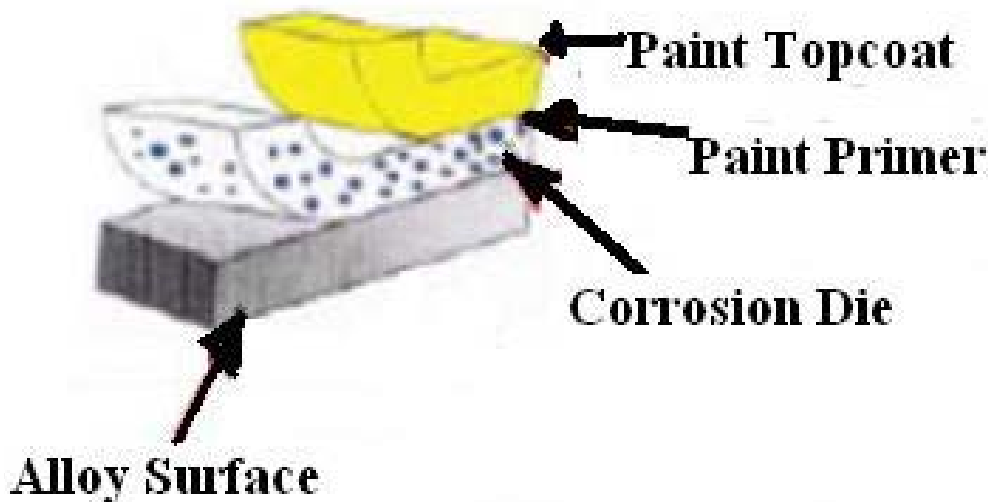


**Figure 1:** a chain transition between extended and compacted coil states to represent the smart behavior correspond to polymeric chains and crosslinking points respectively.

A compounds was taken, which show fluorescence in the ultraviolet to near infrared region, have been investigated for their corrosion-sensing capabilities when subjected to the effects of temperature,  $p^H$ , reduction, and reoxidation behavior. Potentially relevant to corrosion sensing of polymeric coatings and paints have been described as their principles, which includes following parameter: (a) Paint systems containing color-changing compounds which responding to  $p^H$  changes, (b) Changes of coating compounds from nonfluorescent to fluorescent states upon oxidation or complexing with metal cations, (c) Release of color dyes containing anticorrosive additives from embedded microcapsules filled with dye and additive following mechanical damage of the capsule coating, (d) Use of pigments that absorb corrosive chemicals or release corrosion inhibiting chemicals with or without color changes.

## **2. Experimental Procedure**

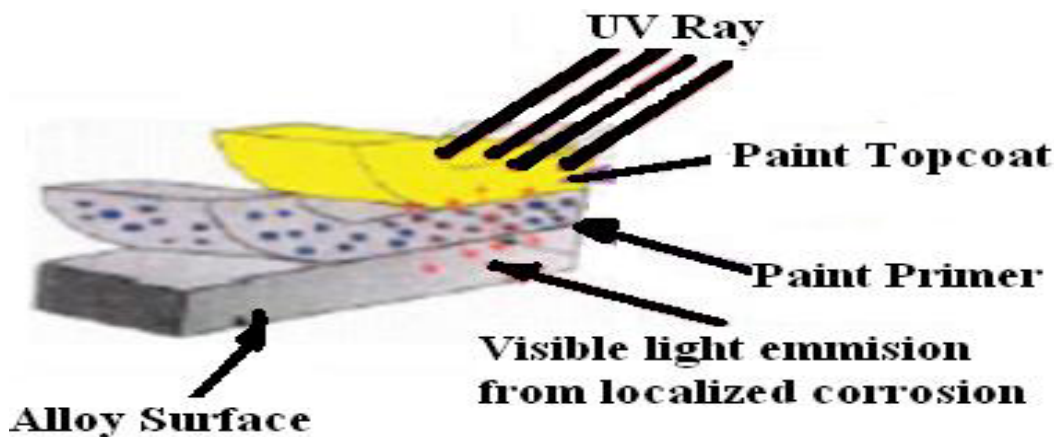
For corrosion sensing, the chemical should fluoresce only when either oxidized or when reacting with the corroding species. Some of compounds, which are experimented for fluoresce with aluminum ions and during oxidation in air when incorporated into primer paint coatings for aluminum alloys are fluorescein, Morin or Schiff bases, oxines and hydroxyquinolines. Fluorescent dyes were applied to microelectronic test vehicles to detect pH changes associated with corrosion of Al or Au metallization. Fluorescing and color-changing dyes also have been applied to Al after corrosion to identify the location of the hydrous aluminum oxide corrosion product. Epoxy coating containing fluorescein on aluminum panels, which experiencing corrosion fluoresces under UV light is shown in figure-2. Aluminum alloys used in aircraft, coated with epoxy-containing fluorescent probes can be scanned with light of suitable wavelength to determine the onset of corrosion.



**Figure 1:** Fluorescent materials coated on Al-alloy.

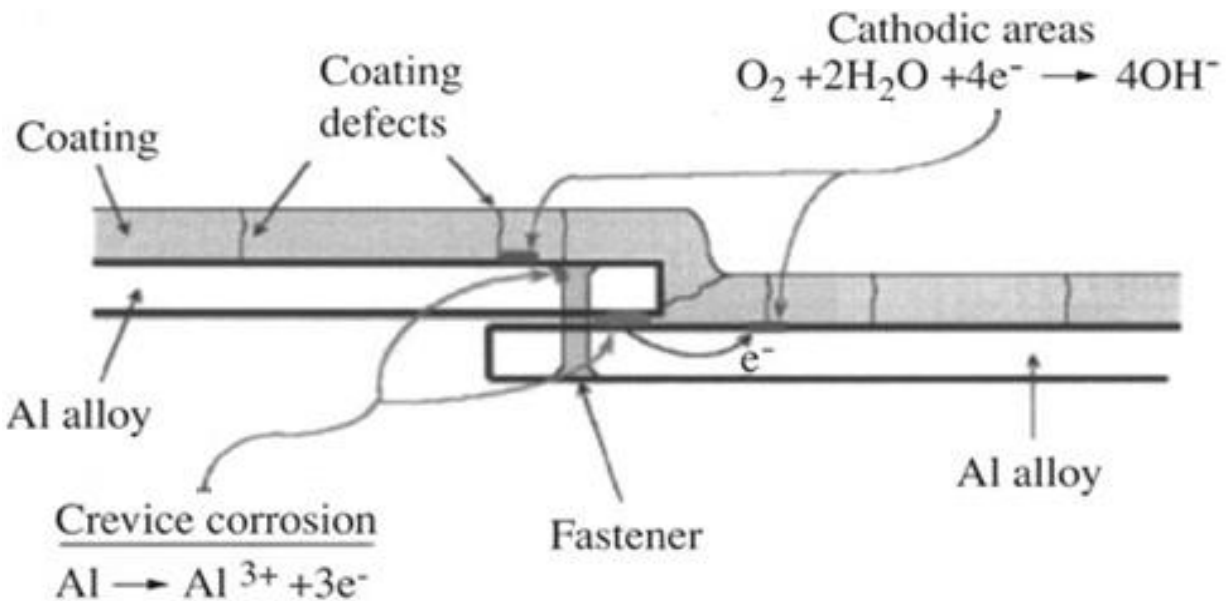
### 3. Results and Discussion

When Al coated material undergo reduction/oxidation behavior, there exist a variety of compounds that change color as a result of pH changes. Zhang and Frankel [7] used different color change or fluorescing compounds, which are sensitive to the increase in local  $p^H$  associated with the cathodic reaction given in reaction(1), accompanying the anodic reaction that forms hydrous aluminum oxide corrosion product.

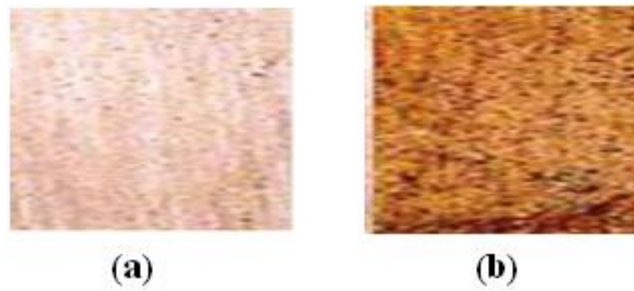


**Figure 2.** Fluorescent materials for corrosion detection on alloy surfaces.

Figure-3 contains a schematic of an experimental painted lap-joint setup for detecting crevice corrosion on aluminum panels and results on panels coated with acrylic paints containing  $p^H$  indicators after immersion in 1 M NaCl solution for a period of time (shown in figure-4a & 4b); color change in the coating indicated the occurrence of localized corrosion. In another approach [8],  $p^H$  sensitive dyes have been encapsulated in a polymeric shell susceptible to degradation at the alkaline  $p^H$  accompanying cathodic corrosion. The released dyes serve as corrosion indicators at the localized corrosion sites. Fiber-optic arrays have been evaluated for corrosion sensing of uncoated or coated aeronautic structures [9-10]. By measuring local chemical concentrations at these sites, the results were applied to real-time corrosion such as galvanic and crevice corrosion and pitting.

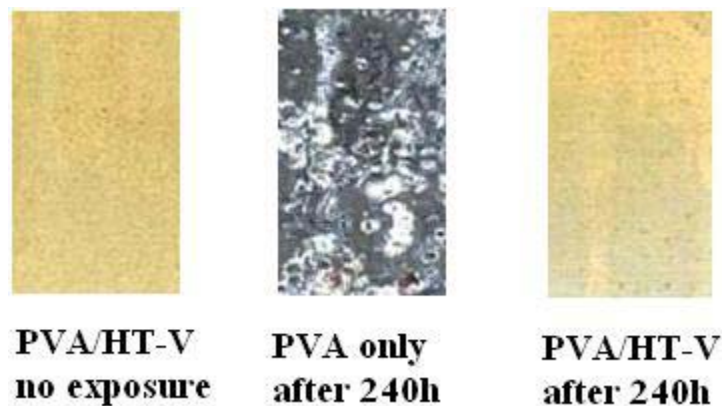


**Figure 3.** Experimental setup for determining crevice corrosion through color changes in painted lap joint.

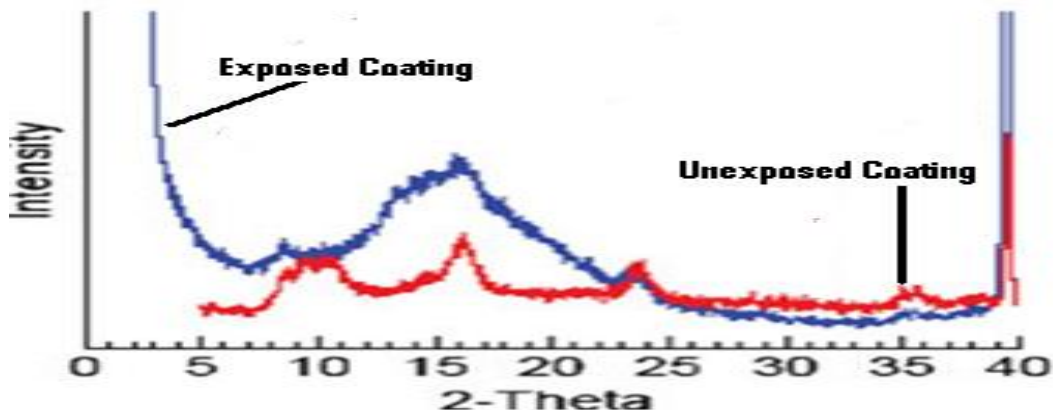


**Figure 4. surface morphology of** color change of two  $p^H$  sensing coating on Al substrate following immersion in 1.0 M NaCl solution. (a) phenolphthalein paint after 8 days and (b) Bromothymol paint after 13 days.

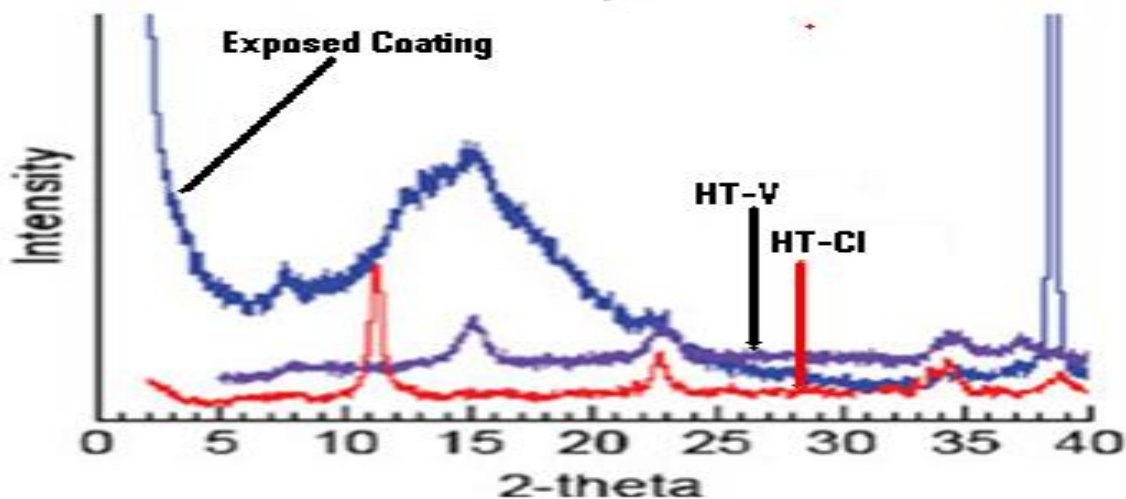
Recently, anion-exchanging hydrotalcite and cation-exchanging bentonite clays, both modified through the incorporation of specific ions, were used in organic coatings for corrosion protection and sensing [11]. It was shown that a change in crystalline structure identified by X-ray diffraction could be detected as a result of an ion exchange reaction accompanying corrosion. As shown in Figure- 5, the coatings with a decavanadate modified hydrotalcite (HT-V) show better protection in the salt spray test than the unmodified coating. Figure-6 & -7 compares the X-ray diffraction patterns of epoxy containing HT-V deposited on aluminum before and after exposure in a 0.5 M NaCl solution for 450 h.



**Figure 5.** Optical macrographs of 2024-T3 coupons coated with PVA with and without HT-V inhibitors before and after exposure to ASTM B117 salt spray.



**Figure 6** X-ray diffraction patterns of epoxy containing HT-V deposited on aluminum before exposure in a 0.5 M NaCl solution for 450 h.



**Figure 7.** X-ray diffraction patterns of epoxy containing HT-V deposited on aluminum after exposure in a 0.5 M NaCl solution for 450 h.

#### 4. Conclusions

Fluorescein, Morin or Schiff bases, oxines and hydroxyquinolines fluoresce are used for Al-alloys for detection of oxidation/ corrosion in its surroundings. Another important element of a smart material is that the action of receiving stimuli and responding to the stimuli to produce a useful effect is that it must be reversible.

## 5. References

- [1] J. A. Harvey, Kirk-Othmer Encyclopedia of Chemical Technology, 4th Ed., Supplement, John Wiley, 1998, 502-504.
- [2]<http://www.plastemart.com/upload/literature/smart-polymers-shape-memory-aircraft-automotive-medical-textile-good-growth.asp>
- [3] <http://www.nuffieldfoundation.org/practical-chemistry>
- [4] Chunye Xu, Chao Ma, Minoru Taya, Patent application title: Smart Sunglasses, Helmet Faceshields and Goggles Based On Electrochromic Polymers. Patent application number: 20080239452, 2008.
- [5] <http://www.vigyanprasar.gov.in/Radiosericals/Plastics%20by%20Dr%20V.%20P.%20Sharma,%20IITR.pdf>
- [6] S. Mondal, Phase change materials for smart textiles - An overview, Applied Thermal Engineering 28, 2008, 1536-1550
- [7] Frankel, G. S.; Buchheit, R. G.; Zhang, J.; US Patent Appl. US2003/0068824.
- [8] Li, W. Proceedings of the US Army Corrosion Summit 2006, Clearwater Beach, FL, Feb. 14-16, 2006; Session A-Day 2, p. 7; available at [www.armycorrosion.com](http://www.armycorrosion.com).
- [9] Benounis, M.; Jaffrezic-Renault, N. Sensors Actuators B 2004, 100, 1-8.
- [10] Szunerits, S.; Walt, D. R. Anal Chem 2002, 74, 886.
- [11] W. Feng, S. H. Patel, M-Y. Young, J. L. Zunino, Smart Polymeric Coatings—Recent Advances, Advances in Polymer Technology, Vol. 26, No. 1, 2007, 1-13.