Application of Conducting Polymers in Corrosion Protection

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INTRODUCTION

Conducting polymers were rediscovered in the late 1970s, giving material scientists the ability to combine the important electronic and optical properties of semiconductors and metals with the mechanical properties and ease of processing associated with polymers.[1] The interest in the study of conducting polymers has increased dramatically over the past 15 years.[2,3] The advantages of using conducting polymers are that they are light weight, inexpensive and more recently easily processable.[4] The electrical conductivity in these polymers is considered to be intermediate between semi conductors and metals. The conductivity ranges from 1-1000 S/cm. These properties make conducting materials ideal candidates for use in electronic devices, switching devices, rechargeable batteries, sensors, and corrosion inhibitors.

Intrinsically conducting polymers (ICPs) have been identified as novel corrosion inhibiting coatings for metals.[5] Intrinsically conducting polymers are defined as "polymers that conduct electric currents without the addition of conductive (inorganic) substances."[6] Among all the conductive polymers studied so far, polyaniline is the first to achieve commercial availability.

Polyaniline is the oldest known synthetic organic conducting polymer. It was first reported in 1862, by H. Letheby in the *Journal of the Chemical Society*. There was little interest in polyaniline until the late 1970s when there was a sudden resurgence in polyanilines research.[7] Polyaniline has been used in rechargeable organic batteries, electrochromic display devices, modified electrodes and as a microelectronics device.[8] Polyanilines are relatively easy to synthesize and can be prepared either chemically or electrochemically.[9]

Standard coating systems for metal protection incorporate more than one type of coating system.[5] A common first step in any coating process is usually the application of a corrosion inhibitive metal oxide such as chromate or molybdate on the surface of the substrate. The next step is the application of a primer which contains corrosion inhibitors that cathodically protect the metal substrate, for example, a zinc rich primer. The final step is usually the application of a barrier coating which shields the primer coating from the environment. The

The use of oxides, such as chromates, is highly effective in corrosion protection. Scientists are looking at alternative materials to replace environmentally hazardous materials, e.g., chromates. One of the group of materials identified as corrosion inhibiting are intrinsically conducting polymers.

This paper focuses on the use of ICPs as a possible corrosion inhibitive substance. This paper also reviews literature on the research of different groups on the use of polyaniline and other conducting polymers as corrosion inhibitors. Intrinsically conducting polymers, especially poly-aniline, are being studied with great interest. Studies indicate that they have the potential of replacing some of the currently available materials.

use of oxides such as primer chromates are highly effective, but pose potential environmental hazards.

This paper focuses on the use of ICPs as a possible corrosion inhibitive substance. ICPs such as polyaniline, polypyrrole, etc., conduct electrons due to the presence of conjugated double bonds in the structure. The high electron mobility in conducting polymers is due to the fact that in a conjugated system of electrons, considerable delocalization of the electrons is achieved along with polymer chains.[9]

ICPs are believed to passivate metals by forming a protective oxide on the surface of the metal, thereby reducing corrosion.[5] DeBerry was the first to indicate the use of a conducting polymer in corrosion inhibition.[10] One of the key features that he suggested was the possibility of the protection of the substrate where defects in the coatings existed. The basis for this argument was

that, since ICPs are conductive, the entire coating would act to passivate any area of the exposed metal.[5]

ICPs are technologically important because of the following properties. Polyaniline is considered to be a synthetic metal. While its specific conductivity and the temperature dependence of its conductivity are considered semi-metallic, properties such as thermopower fall in the metallic region. The mechanism of conductivity in polyaniline is electronic in nature, which is analogous to the mechanism in metals. Polyaniline can be solution processable, a very important characteristic not available with most other conducting polymers. Polyaniline is green in its doped form and can change color when exposed to a variety of substances. The 'doping' process creates charge carriers by adding electrons to the conduction band or removing electrons from the valence band of the polymer. Doping can be carried out either with a gaseous dopant, with the dopant in solution, or by electrochemical oxidation or reduction. Polyaniline is a reactive polymer, but as a metal it is more noble than iron or copper. It can undergo reproducible chemical or electrolytic "switching" between the different conducting states of the polymer.

Considerable interest has been generated in the research of potential applications for polyaniline. Some of the possible applications foreseen for this polymer are EMI shielding, preparation of dispersions of polyaniline in organic solvents to produce transparent ultra-thin layers on different substrates, electrically conductive surface coatings, electronic functional layers, corrosion protection, sensors, membranes for gas separation, transparent electrodes, smart windows, and electrochromic displays. This paper reviews literature on the research of different groups on the potential use of polyaniline and other conducting polymers as corrosion inhibitors.

Conducting Polymers and Corrosion

DeBerry and Viehback[10] were among the first to report the possibility of using polyaniline as an electroactive coating on active/passive metals. This electroactive coating, they claimed, maintained stainless steel in the passive state potential region. The passive film behaved like a very non-ideal semi-conductor with respect to charge transfer mediation between the metal and the electroactive film. Anodically deposited polyaniline films were able to protect steels in a sulfuric acid medium by maintaining the metal in the passive state and repassivating the damaged areas.

In another paper[11] DeBerry discussed the modification of the electrochemical and corrosion behavior of steel using an electroactive coating. He used polyaniline as the primary electroactive material in preparing coatings for 400 series stainless steels. The advantage of polyaniline was its effective use in acidic environments. Hydrogen ion is the preferred counter-ion for polyaniline since it maintains its electoneutrality during electron transfer. He reported rates of corrosion of 3.1×10^4 μm/yr for bare stainless steel and less than 25 μm/yr for polyaniline coated stainless steel specimens. The coatings removed from the deposition bath were initially blue-black in color. On placing the sample in an acid environment, the coating color changed to green. The open circuit voltage decreased from 0.6V to 0.2V when the color change was observed.[11] As the electrode failed, the color change became a lighter green and became transparent before becoming active. Extended exposure led to disbonding due to the evolution of hydrogen. Bare stainless steel specimens became active in minutes when placed at open circuit voltage in an acid solution. Polyaniline coated samples remained passive for several hours before becoming active.

Corrosion measurements of polyaniline coated steel panels in a solution containing 0.2M NaCl and 0.2M H_2SO_4 showed unusual oscillations at the open circuit potential. When the solution was changed to only 0.2M H_2SO_4, the oscillations stopped. The interpretation given was that for the coated electrode, the passive film periodically underwent partial breakdown in the "acidic chloride" solution. The passive layer was then reformed with the dopant acid of the polyaniline. Visual observation of this effect was the change in color of the electrode. The color of the electrode changed from clear to pale green. After repassivation, the color changed from green to dark green. He thus showed that stainless steel electrodes coated with thin films of polyaniline remained passive for long periods of time in acid solutions. N. Ahmad et al.[12] reported that steels coated with the emeraldine base form of polyaniline had the capability of anodically passivating steels in certain corrosive environments.

Smyrl et al.[13,14] describe a method to stabilize the potential well of the metal in the passive region when it is covered with an oxide film using electroactive coatings. They demonstrate the feasibility of using electroactive coatings in corrosion protection. They proposed that the redox polymer film would keep the potential of the metal surface (covered with the oxide layer) between the active and trans-passive potential regions. The authors electrochemically deposited poly(3-methylthiophene) on Ti/TiO_2 substrates by anodic electropolymerization. This coating was shown to control the potential of the metal in the passive region. The film does not remain active if the film is reduced. For this process to work, galvanic coupling was necessary to hold the potential of the metal in the passive region. The authors mention that oxygen reduction on the film is necessary to hold the potential in the required region. Introduction of platinum particles in the conductive polymer film improved the oxygen reduction kinetics. The oxygen reduction was fast enough to maintain the passivation current and keep the metal passive, thereby protecting it from corrosion. However, the authors state that the films of poly(3-methylthiophene) were not stable enough for long term use. Thus, the role of the conducting polymer film was to 'poise' the potential of the oxide-covered metal in the passive region. The conducting polymer film does this by maintaining a current between the passive surface and the reduction reaction occurring on the surface of the polymer film. However, the film cannot remain active if the polymer is reduced. This is compensated by the oxygen reduction reaction. The oxygen reduction was catalyzed by incorporating platinum particles in the polymer film.

Thompson et al.[15] in a joint research effort involving NASA and the Los Alamos National Laboratory reported the use of corrosion protective coatings using electrically conducting polymers for metal surfaces. Electrically conductive polymer coatings were developed which imparted corrosion resistance to saline and acidic environments. They claimed these coatings imparted corrosion resistance to the metal where scratches existed in the protective coating. The team of researchers studied several conducting polymers such as polyaniline, poly(3-hexyl thiophene), poly(3-thienyl methylacetate) and poly(3-thienyl ethylacetate). Of the different polymers studied, polyaniline was found to have the best overall properties and hence was selected for further study. Polyaniline was synthesized by the chemical polymerization of aniline in the presence of an oxidizing agent like ammonium persulfate. The emeraldine base was applied from solution onto steel panels and then doped with species such as p-toluene sulfonic acid, tetracyanoethylene (TCNE), and zinc nitrate. After doping, a coating of epoxy cured with an amine hardener was applied on top of the polyaniline coating. They claimed this coating had the necessary 'electronic environment' and 'coating toughness and resistance' to harsh environmental conditions. Corrosion testing was performed in 3.5% aerated NaCl and 0.1M hydrochloric acid solutions. Along with these specimens they also tested a series of specimens without any conductive polymer present. Samples with the conductive polymer basecoat and epoxy topcoat (unscribed) showed no corrosion in 3.5% NaCl solution after 12 weeks. The control sample, however, showed a significant amount of corrosion. The samples with the conductive polymer basecoat and epoxy topcoat (scribed) immersed in aerated hydrochloric acid solution showed no corrosion after 12 weeks. The scratched surface still appeared to be 'shiny' after 12 weeks of exposure. On-site testing of polyaniline primers topcoated with polyurethane coatings indicated that there was no visual change in the coating containing the polyaniline basecoat. The control sample without the polyaniline treatment showed significant corrosion. The authors recommended these coatings for applications on equipment exposed to heat, sunlight, saline environments, and other outdoor exposure concerns, coatings for bridges, coatings for rebar in concrete, coatings for underground storage tanks, and coatings for the automotive industry.

Beck[16] described a method of electrochemically depositing polypyrolle on substrates such as aluminum and steel. He proposed that the heteroaromatic structures in conducting polymers allowed their use as protective coatings in corrosion inhibition. The cited advantages of using these materials in corrosion inhibition were flexibility, insolubility, and adhesion to the substrates.

Troch-Nagels et al.[17] electrochemically deposited conducting polymers on mild steel by the electropolymerization. Their aim was to coat mild steel with a conducting polymer which would retard electrochemical corrosion of the metal by introducing another electrochemical reaction at the surface of the film. The polymers studied were polyaniline and polypyrolle. Several

electrolytes were studied for the electrochemical synthesis of polyaniline on mild steel. In basic solutions, brown films were obtained which non-homogeneous. The films were insulating and did not change when dipped in sulfuric acid. This phenomenon was also observed when the synthesis was carried out in neutral solutions. In an acid solution such as 20 vol% CH_3OH, 0.13M H_2SO_4 and 0.3M aniline, the films obtained were black and powdery. The aniline oxidation started at 800mV/SCE. Below 800mV/SCE, no films were obtained and above 1400mV/SCE, the films did not have good properties. The optimum current density was between 0.05 to 0.3 A dm^{-2}. The lowest values of current density were found to give the best films. Since the sulfuric acid solution did not give the expected results, the solution was changed to nitric acid (0.1M HNO_3, 0.3M aniline). With this solution, the aniline oxidation occurred at the same potential as for the sulfate solution and the dissolution of the substrate decreased. The properties of films obtained in nitric acid solutions were summarized as followed:

(1) The films were powdery even after curing at 170°C for 10 minutes.

(2) SEM micrographs showed good surface structure.

(3) Films were brittle.

(4) Conductivities were low.

(5) Substrate dissolution was decreased, but only marginally.

(6) Painting of the coated substrates was not possible by anaphoresis (e-coat). The films obtained were insulating.

They thus concluded that polyaniline films did not meet the requirements for mild steel protection and polyaniline did not increase the corrosion resistance of the substrate. Their results using polypyrolle indicated that it was a better candidate than polyaniline and films obtained in neutral solutions were sufficiently conductive to allow anaphoretic painting. The corrosion resistance of the substrates was substantially increased. The adhesion and mechanical properties remained a problem. Sekine et al.[18] also found that electrochemically deposited polyaniline was not very useful in corrosion protection. Another study by Sathiyanarayan[19] showed that soluble poly(ethoxy aniline) acted to reduce the corrosion of iron in a 1N hydrochloric acid solution. Geskin[20] was the first to report a successful electrochemical synthesis of polyaniline, using a nickel substrate. In the absence of polyaniline, the bare metal electrode dissolved rapidly in an acid solution but the rate decreased when a polyaniline/nickel electrode was used.

Wessling[21] used a different approach to coating the metals with polyaniline. Previous studies had all tried to incorporate polyaniline eletrochemically. His objective was to coat metals such as iron, steel and stainless steel non-electrochemically by using polyaniline dispersions or polyaniline containing lacquers. His initial experiments showed some improvement in corrosion protection, but the effects observed in a practical test such as salt spray were not totally convincing. The polyaniline used in his studies was manufactured by Allied Signal Company under the trademark of Versicon®. After suitable pretreatment, the polyaniline coating process was

Table 1—Summary of Corrosion Results for Coatings Incorporating Polyaniline on Untreated Steel

Description of Coating System	Formulation	Rating of Failure D-1654 A
Versicon® blend in		
Polyamide cured epoxy	PA-30 AmideB	7
Polyamine cured epoxy	PA-30 AmineB	5
Panda blend in		
Polyamide cured epoxy	Panda-30 Amide B	7
Polyamine cured epoxy	Panda-30 Amine B	7
Aroflint system	Panda-30 AroG	5
Acrylic/Melamine	Panda-30 ACMEG	6
Acrylic/Polyurethane	Panda-30 ACPUG	6
Panda basecoat with clear topcoat of		
Aroflint system	PANBC+AROTO	9+
Acrylic/Melamine	PANBC+METC	9
Acrylic/Polyurethane	PANBC+PUTC	9
Control Systems		
Polyamide cured epoxy	Control Amide	7
Polyamine cured epoxy	Control Amine	7
Aroflint system	Control Aro	0
Acrylic/Melamine	Control ACME	2
Acrylic/Polyurethane	Control ACPU	6

Data represents the salt spray results obtained for the coatings on steel after testing for 500 hours in the salt fog cabinet. The test was performed and the ratings were determined according to the ASTM Standard Test Methods for evaluations (ASTM B 117-90, ASTM D1654-92 and ASTM D3359-92a). Data represents the extent of corrosion in a scribed sample. Based on the extent of corrosion, the rating was assigned from 10 = no corrosion to 0 = extreme corrosion.

polyaniline (Versicon®) was applied to the substrate from a solution in dimethyl propylene urea or N-methyl pyrollidone. The neutral polyaniline was then doped in an aqueous solution of p-toluene sulfonic acid for 4 to 24 hr. The samples were top-coated with an epoxy system. A scribe/damage was simulated by drilling a precise hole in the specimen. A control epoxy, a neutral polyaniline coating topcoated with epoxy and a doped polyaniline coating topcoated with epoxy were studied. Visual and electrochemical results indicated polyaniline affected the corrosion process. Both doped and neutral polyanilines exhibited corrosion protection. In the acid medium, the doped polyaniline sample showed greater shift, while in the NaCl medium, the neutral sample showed a greater shift in corrosion potential. The samples in the acid medium showed a shift to a more noble potential while the NaCl samples showed shifts to a more active potential.

Corrosion rate measurements showed a decrease in corrosion rate for the samples treated with polyaniline. The effect on the corrosion rate reduction for the doped polyaniline was greater in the acid solution, and the neutral polyaniline had a greater rate reduction in the NaCl solutions. The results mentioned previously were for the scribed samples. In samples where the metal surface was not exposed, the doped polyaniline exhibited better corrosion protection than the neutral system. The results indicate significant corrosion protection provided to scratched areas galvanically coupled to polyaniline coatings and that the extent of protection depended upon both forms of polyaniline (doped, undoped) as well as the nature of the corrosion environment. The data presented indicate that the polyaniline coating caused the metal to form a passive oxide layer on the surface in an acid environment. However, this effect was not observed in NaCl solutions. XPS and Auger studies indicated the passive oxide layer was composed of γ Fe_2O_3 on the outside with an Fe_3O_4 layer sandwiched between the passive oxide layer and the nascent metal.

Jasty and Epstein reported that the neutral emeraldine base form of polyaniline passivated all forms of iron when exposed to corrosive environments.[23] The passivation was found to occur by the formation of a thin passive oxide layer consisting mainly of hematite. They found that the emeraldine base passivated the surface of iron even when applied as an undercoat. However, they found that the emeraldine hydrochloride does not provide effective corrosion protection for iron.

Wei et al. in another study performed a series of

applied by a dip process. The coating was made in a series of steps to obtain the appropriate film thickness. The coating process was repeated at least five times (after complete drying of the previous coating step) to a maximum of 20 times to increase thickness. The corrosion potential measurements were made in 1M NaCl solution. He observed a significant and reproducible shift of the corrosion potential and also a reduction in the specific corrosion current or corrosion rate. Visual observations indicated a change in the optical appearance of the metal surface after removal of the polyaniline coating. While the original metal appeared shiny, after coating with polyaniline, the metal surface appeared light to dark grey, mat, and spotted.

The mechanism of the passivation of iron by polyaniline proposed was as follows: the first step of the interaction between polyaniline and iron was an etching step. The polyaniline removes the first few layers of iron and dirt. The fresh iron layer formed then is coated with an oxide layer. The experimental evidence for this was the elemental analysis performed on the pure iron, iron freshly treated with polyaniline and the passivated areas. The pure iron showed no oxygen content, while the freshly etched areas showed some oxygen and the passivated areas showed large amounts of oxygen. He therefore concluded that proper coating of metals with pure polyaniline can lead to a significant shift of corrosion potential to decrease the corrosion rate of the metal.

Lu, Elsenbaumer and Wessling[22] in another study, evaluated the anti-corrosion behavior of polyaniline exposed to dilute acid and salt solutions. Mild steel specimens when coated with polyaniline and overcoated with epoxy barrier paint showed a reduction in the corrosion rates of about 1000 orders of magnitude in 0.1N HCl and 10 orders of magnitude in 3.5% NaCl. Neutralized

electrochemical corrosion measurements on polyaniline coated steel specimens.[24] It was found that the base form of polyaniline offered better corrosion protection in aqueous NaCl solution. They observed an increase in the corrosion potential and corrosion resistance and a decrease in the corrosion current when compared to the uncoated specimen. They found that the polyaniline base with a zinc nitrate treatment followed by an epoxy topcoat exhibited the best overall protection.

Sitaram, et al. conducted corrosion studies on coated steel specimens and *Table* 1 describes the salt spray results.[25] The polyanilines studied were the Versicon polyaniline, Versicon polyaniline base (prepared by neutralizing the Versicon polyaniline with ammonium hydroxide) and Panda (synthesized at the laboratories of Monsanto Co.). The results indicate that Panda exhibits significant improvement in the corrosion protection of steel when applied as a basecoat followed by a clear topcoat of a conventional coating system. Three different types of topcoats were evaluated. All three systems, exhibited better corrosion protection than the conventional systems studied. However, the Panda or the Versicon did not exhibit significant protection when blended into conventional formulations indicating it did not function as a pigment. The corrosion protection was either comparable or lower than observed for the control samples. For all the systems with the Panda basecoat, some corrosion was observed in the scribe. The extent of corrosion was significantly lower than that observed for the control samples.

SUMMARY

The results reported by various research groups on the application of conducting polymers in corrosion protection have shown polyaniline to be the most promising candidate among all the polymers studied. The polyaniline helps in corrosion protection by forming a passive protective oxide on the surface of the metal. The polyaniline/ICP helps in maintaining the passive oxide on the surface thereby protecting the substrate from further corrosion. Initial results in our laboratory indicate that the polyaniline has better corrosion protective properties when applied as a coating on the metal.

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