

Corrosion Protection Of Mild Steel By Coatings Containing Polyaniline

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Abstract

The anti-corrosion performance of polyaniline coated mild steel samples exposed to artificial brine and dilute hydrochloric acid environments was evaluated. Samples of mild steel (UNS G10100) coated with polyaniline deposited from solution, and overcoated with an epoxy barrier paint, when scratched to expose precise areas of bare metal, exhibited corrosion rates in aqueous 3.5% NaCl solutions 2 times less, and in 0.1 N HCl solutions, 100 times less than observed on identical samples coated with epoxy paint alone. Mechanistic information, and quantitative corrosion rates were obtained by Tafel Extrapolation, Potentiodynamic Polarization, Galvanic Coupling and Electrochemical Impedance Spectroscopic techniques. These studies, in conjunction with surface analysis by ESCA and Auger techniques, indicate that the corrosion protection, even for exposed bare steel areas, occurs by the formation of passivating iron oxide (γ -Fe₂O₃ and Fe₃O₄) surface layers. The formation of these specific oxide layers occurs when the polyaniline is galvanically coupled to the steel. This is evident by the fact that the dimensions of the exposed bare steel area that can be protected in a scratch can be large, but are limited in each corrosion environment.

INTRODUCTION

The possibility for anodic protection of steel and other metals was proposed over 10 years ago by MacDiarmid [1]. In 1985 DeBerry [2] found that polyaniline electrochemically deposited on ferritic stainless steels (410 and 430) provided a form of anodic protection that significantly reduced corrosion rates in sulfuric acid solutions. The electrochemical deposition of PANi was preceded by the formation of a passive oxide layer on the steel surface. The doped PANi layer in electrochemical contact with the steel stabilized the passive oxide layer against dissolution and reduction. More recent studies by Troch-Nagels *et al* [3] on the electrochemical deposition of PANi and polypyrrole on mild steel showed that PANi provided no corrosion resistance, but polypyrrole did. Sekine *et al* [4] also found that electrochemically deposited PANi provided very little corrosion protection to mild steel surfaces. Sathyanarayanan *et al* [5] found that soluble poly(ethoxyaniline) acted to inhibit the corrosion of iron in 1 N HCl solution. Corrosion inhibition by the polymer in solution was about 8 times more effective than aniline at concentrations of 75–100 ppm. Significant corrosion inhibition of mild steel exposed to saline (3.5% NaCl) and acidic (0.1 N HCl) environments was reportedly obtained by Thompson *et al* [6] for samples solution coated with polyaniline. These polyaniline coatings seemed to promote corrosion protection even where scratches existed in the protective coating. Wessling [7] just recently reported that mild steel, stainless steel, and copper were all found to passivate by repeatedly dipping clean surfaces of the metals into dispersions of doped polyaniline (VersiconTM [8]). The dip coating process was repeated from 5

to 20 times to increase the thickness of the polyaniline layer. Passivation was found to occur by the formation of an oxide layer on mild steel induced by contact with the polyaniline. This was evident by removal of the polyaniline layer which revealed a gray matted surface and persistent passivated behavior.

The intriguing findings of Thompson [6] and Wessling [7] prompted us to investigate the mechanisms of corrosion protection of mild steel provided by both doped and undoped forms of polyaniline in brine solutions and in dilute hydrochloric acid. We were especially interested in characterizing the mechanism of protection, if any, in exposed bare steel areas (scratches) on coated samples. It was also our intent to quantitatively characterize the levels of corrosion protection, as well as determine the limiting dimensions of a scratch in the coatings that would be passivated under the various corrosion conditions.

EXPERIMENTAL

Square (2"x2"x0.0625") mild steel coupons (C1010, UNS G10100) from Corrosion Test Supplies, Inc., were prepared by sanding with emery paper to 600 grit, then degreased with hot xylene and acetone, then dried in a desiccator. Neutral polyaniline coatings were applied to the clean steel surfaces as a 10% solution of neutralized VersiconTM in dimethyl propylene urea [9] or NMP. The polyaniline coatings were allowed to dry in air at room temperature for several days. Experiments in which doped polyaniline was used, the coated samples were exposed to an aqueous solution of p-toluene sulfonic acid

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for 4 to 24 hrs., rinsed with distilled water, then air dried. All samples were then topcoated with a curable epoxy resin (Ciba-Geigy Araldite™ GY2600) as a thick barrier layer. To study the corrosion characteristics for precise areas of exposed bare steel, a precision hole was drilled just through the epoxy and polyaniline layers in each sample exposing clean metal surfaces (no oils were used). Control samples were prepared as above but without the polyaniline layer.

Electrochemical corrosion measurements on the exposed steel surfaces were performed using an electrochemical cell as schematically shown in Figure 1. The initial corrosion environments were aerated 3.5% NaCl and 0.1 N HCl solutions at room temperature. For DC corrosion measurements, a Gamry Instruments model PC3 potentiostat/Galvanostat/Zero Resistance Ammeter with Gamry Instruments CMS 100 and CMS 300 corrosion system software running on a personal computer was used. Electrochemical Impedance measurements were carried out using a Stanford Research Systems SR 830 lock-in amplifier connected to the above potentiostat.

The passivating metal oxide layers were characterized by scanning electron microscopy (SEM), by x-ray photoelectron spectroscopy (XPS), (Perkin Elmer Phi 5000) and by scanning Auger spectroscopy (Fison-VG XSAM-800) (SAM).

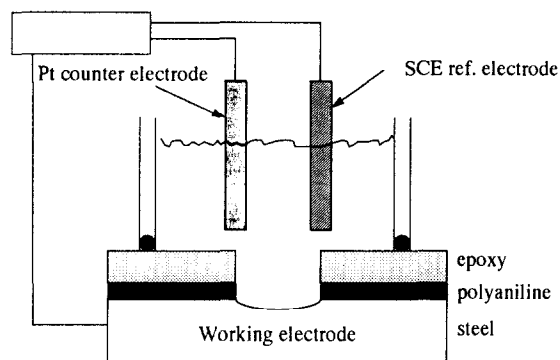


Figure 1. Schematic of the test electrochemical corrosion cell

RESULTS AND DISCUSSION

For our studies we chose three standard sample configurations for ambient exposure in neutral aerated 3.5% sodium chloride solutions and in 0.1 N HCl solutions. The first sample configuration was a mild steel coupon coated only with epoxy paint. A hole 1.2 mm in diameter was drilled just through the coating (exposing clean bare steel) in the center of the coupon (D,e/s). This served as the control sample for each experiment. The next sample configuration was a steel coupon first coated with neutral polyaniline then with an epoxy overcoat. The same diameter hole was drilled just through the coatings to expose the same surface area of steel as with the control (D,e/nP/s). The third sample configuration was a steel coupon first coated with toluene sulfonic acid doped polyaniline then overcoated with epoxy paint. This sample also had the same diameter hole drilled through the coating layers as the above two samples (D,e/dP/s). Thus, all three sample configurations have the same exposed area of bare steel, but different coatings. These samples were exposed to the two corrosion environments for a total of eight weeks using

the corrosion cell configuration shown in Figure 1 with the exposed steel area located in the center of the cell. Corrosion measurements were made on the samples during the test period.

Visual observations made on the samples after eight weeks exposure are summarized in Table 1. It can be seen that of the samples exposed to HCl, the samples containing polyaniline were considerably protected against corrosion (rust). For the samples exposed to NaCl, the corrosion protection provided by polyaniline appeared to be less than that provided in the HCl environment, yet significant compared to the control sample, which severely corroded within a few hours.

Table 1
Summary of visual observation during the corrosion tests.

	initial stage (2 hrs to 3 days)	intermediate stage (1 to 5 weeks)	final stage (8 weeks)
0.1 N HCl			
D, e/s	surface became black at 1 to 2 days	considerable rust and filiform corrosion	underfilm rusting
D, e/dP/s	shiny surface	still shiny	bare steel covered by deep gray-black thin film with some shiny steel surfaces
D, e/nP/s	dim gray	small brown spots at several areas	mild rust
3.5 % NaCl			
D, e/s	rust at 3 hrs	serious corrosion over epoxy film	voluminous rust
D, e/dP/s	light brown/black film	very rusty	mild attack to epoxy layer
D, e/nP/s	shiny with white-gray film	thin light-brown film over bare steel	mild attack on bare steel, some attack at epoxy surface

In addition to visual observations, several corrosion measurements were made during the exposure periods. Measurements of corrosion potential relative to E_{SCE} provide an indication that the presence of polyaniline on steel affects the corrosion process. Table 2 lists corrosion potentials at various times for samples exposed to the two test environments. Several interesting features are evident: 1) in all cases, except the sample containing neutral polyaniline in HCl, after 8 weeks exposure the samples containing polyaniline exhibited corrosion potentials more noble than the corresponding control sample, 2) the largest shifts in corrosion potential with exposure time were observed for the sample containing doped polyaniline in HCl and neutral polyaniline in NaCl, and 3) all samples in the HCl environment showed shifts to slightly more noble potentials with time, while those in NaCl showed shifts to more active potentials with exposure time. While these measurements indicate potential changes in corrosion behavior, these thermodynamic measurements do not provide information on corrosion rates.

Corrosion rate (current) information can be obtained by the Tafel extrapolation method, where large cathodic and anodic polarizations provide the cathodic and anodic polarization curves for the respective corrosion processes [10]. Extrapolation of these curves to their point of intersection provides both the corrosion potential and the corrosion current. Tafel measurements for the three samples configurations in HCl after 8 weeks exposure are shown in Figure 2 and those for samples in NaCl are shown in figure 3. Table 3 summarizes the corrosion rates observed from the Tafel measurements after 8 weeks.

Table 2
Corrosion potential measurements versus SCE

	0.1 M HCl	3.5 % NaCl
	E _{corr}	E _{corr}
Drilled epoxy/C1010, 1 hour	-0.54	-0.64
day 1	-0.57	-0.70
Week 8	-0.59	-0.62
Drilled epoxy/neutral PANi/C1010, 1 hour	-0.56	-0.88
day 1	-0.57	-0.82
Week 8	-0.58	-0.82
Drilled epoxy/doped PANi/C1010, 1 hour	-0.58	-0.87
day 1	-0.59	-0.82
Week 8	-0.65	-0.85

The Tafel measurements clearly show that a substantial reduction in corrosion current (rate) occurs for the sample containing doped polyaniline in HCl and for the sample containing neutral polyaniline in the NaCl environment. These measurements corroborate the qualitative findings of Thompson *et al* [6] for exposure of polyaniline coated mild steel samples with a scratch exposing bare steel in similar environments

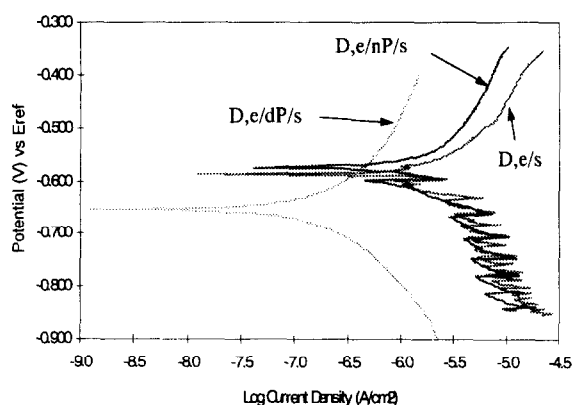


Figure 2. Tafel measurements in HCl.

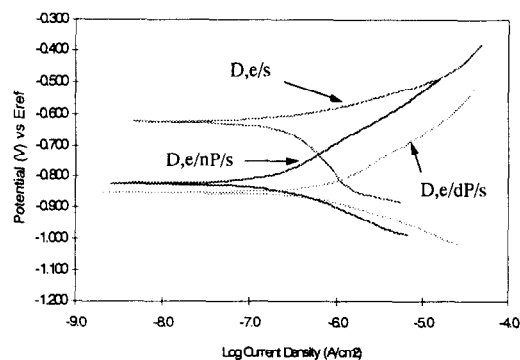


Figure 3. Tafel measurements in NaCl.

Table 3
Corrosion rates after 8 weeks exposure determined by Tafel measurements.

	dilute HCl	seawater
	> 50 mpy	> 20 mpy to > 50 mpy
carbon steel	> 50 mpy	< 20 mpy
316 stainless steel	> 50 mpy	< 20 mpy

	0.1 N HCl	week 8	3.5 % NaCl	week 8
	day 0		day 0	
D,e/s	0.06	8.20	0.018	0.21
D,e/dP/s	0.05	0.19	0.002	0.36
D,e/nP/s	0.15	1.32	0.002	0.12

The results of Wessling [7], and our microscopic observations of the corrosion products on the bare steel surfaces, suggest that the corrosion protection results from the formation of a passivating oxide layer. Potentiodynamic polarization measurements provide a measure of the tendency of an alloy to undergo active/passive behavior. Potentiodynamic measurements for the three samples in HCl and NaCl are shown in Figures 4 and 5, respectively.

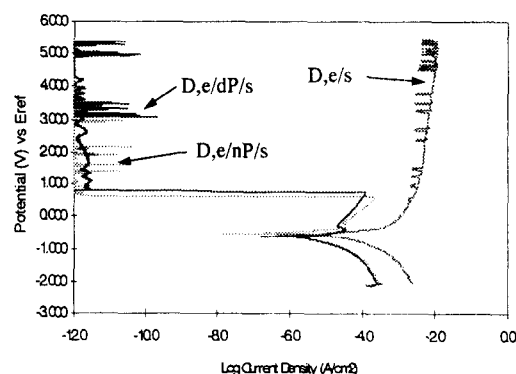


Figure 4. Potentiodynamic measurements in HCl

The curves in Figure 4 clearly shown the tendency for the formation of a passive oxide layer for the samples containing polyaniline, while there is no tendency for passivation with the control sample. It is also clear that with the formation of the oxide layer, corrosion rates decrease by over 10 orders of magnitude! The samples in NaCl exhibit interesting behavior. The samples coated with polyaniline did not exhibit active/passive behavior. Nonetheless, the sample with neutral polyaniline did exhibit a very significant reduction in corrosion current density, as well as very pronounced cathodic and anodic polarization compared to the sample with doped polyaniline and the control sample. These results provide very clear evidence of the significant corrosion protection provided to exposed bare (mild) steel areas galvanically coupled to polyaniline coatings, and that the level of corrosion protection depends both on the form of polyaniline (doped, undoped) and the nature of the corrosion environment.

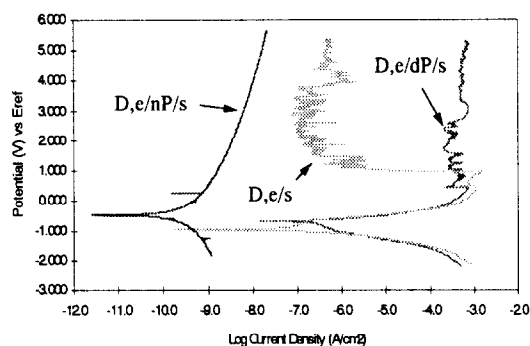


Figure 5. Potentiodynamic measurements in NaCl.

Electrochemical impedance spectroscopic (EIS) measurements confirm the potentiodynamic results. Interestingly, however, EIS measurements on samples without exposed bare steel indicated a reversal in corrosion protection tendency for samples containing doped and undoped polyaniline in NaCl environments. Without bare steel exposed, the sample with doped polyaniline exhibited lower corrosion rates than the sample with neutral polyaniline. Nonetheless, samples containing polyaniline exhibited significant protection over samples without polyaniline coatings.

Visual observation of the corrosion products clearly showed that the samples exhibiting corrosion suppression had a grayish oxide layer form over the bare exposed steel surface, similar to what was observed by Wessling [7] under the polyaniline dispersion coatings on steel. Microscopic examination showed this layer to initially form by growth from the edges of the polyaniline coatings towards the center of the exposed area. With small exposed areas, eventually this oxide growth completely covered the bare steel. With larger exposed areas (diameters), the gray passivating oxide layer extended for only a specified distance from the polyaniline coated edge. Typically, this distance for protection extended to about 2 mm. A significant exception was noted for the samples containing doped polyaniline in HCl. Here, the passivating oxide layer over the bare steel extended at least 6 mm from the edge of the coating.

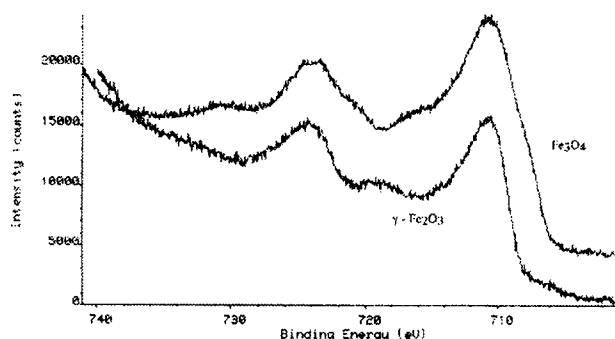


Figure 6. XPS analysis of passive iron oxide layers form in the presence of doped polyaniline.

The chemical nature of the passive oxide layers was determined by ESCA and Auger spectroscopy. Mild steel samples were first coated with a dispersion of doped polyaniline

[7] then exposed to a NaCl corrosion environment for a short period of time. The polyaniline layer was removed and the gray oxide layer was examined by XPS and Auger spectroscopy. The binding energy plots versus intensity for the iron oxide layers on the exterior of the sample and for the oxides right up against the iron surface (examined by ion milling) are shown in Figure 6. These plots indicate that the passive oxide layer is predominately composed of $\gamma\text{-Fe}_2\text{O}_3$ on the outside with a Fe_3O_4 layer sandwiched between this and the nascent steel [11].

CONCLUSIONS

Our studies clearly indicate that polyaniline coatings can provide significant corrosion protection to mild steel exposed to the severe corrosion environments of dilute HCl and NaCl. Further, this corrosion protection extends to exposed areas of bare steel that are galvanically coupled to the polyaniline coated steel. This corrosion protection appears to be electrochemically driven, being derived from both anodic and cathodic polarization. This behavior appears to be unique among the usual mechanisms of corrosion protection provided by other types of corrosion inhibitors.

The level of corrosion protection provided by doped polyaniline to mild steel exposed to dilute HCl is surprising. That this protection extends to bare steel areas is significant and of potential commercial importance. In fact, it appears that the level of protection provided by doped polyaniline is more significant for dilute acid conditions than for neutral saline conditions. It is also evident that the levels of protection provided by polyaniline to steel depend on the form of the polyaniline and the nature of the corrosion environment.

Our results to date were obtained with coatings of polyaniline that exhibited rather poor adhesion to steel substrates. We anticipate even better corrosion protection behavior will be observed with good quality, adherent primer coatings for steel containing polyaniline. These studies are underway with special polyaniline paint formulations supplied by Zipperling Kessler and Co., and our results will be reported at a later date.

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