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# EFFECT OF PHOSPHONIC ACID ANION STRUCTURE ON THE CORROSION INHIBITION OF STEEL BY POLYANILINE

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## INTRODUCTION

Conductive polymers such as polyaniline (PAni) have been examined as candidates for replacing the existing chromate systems. Protonation of emeraldine base creates polarons and bipolarons, single and paired radical cations, respectively, of higher bond energy levels within the molecular orbital band gap.<sup>1</sup> For a conductive coating, considerable delocalization of corrosion charge and potential may be obtained along or between the polymer chains, because of high electron mobility.

Current corrosion systems based on polyaniline typically rely on sulfuric or sulfonic acids as a dopant material, since synthetic techniques utilize persulfates as the oxidant of choice. In our experience, sulfonic/sulfuric acid systems do not produce adequate corrosion protection. However, few studies have been made of alternative dopant anions. Presumably additional studies are deemed of limited benefit because the persulfate synthesis is prevalent and time intensive purifications are required for replacing an existing sulfonic/sulfuric dopant anion. A dopant study could yet be important to achieving a more efficient inhibition system.<sup>2</sup>

Phosphonates are derivatives of phosphonic acids that contain direct phosphorous-to-carbon bonds (P-C). The P-C bonds are more resistant to hydrolysis than the P-O-C bonds of organic phosphates.<sup>3</sup> Phosphonic acids are used as scale inhibitors in aqueous systems. The use of these acids as dopants in polyaniline could improve corrosion protection exhibited by polyaniline. Kinlen et al.<sup>4</sup> have reported that phosphonic acid doped polyaniline in polyvinylbutyral latex coatings showed decreasing galvanic activity with time, providing pinhole passivation. We report testing of an identical series of doped polyanilines as that of Kinlen, et al. applied in an epoxy polyamide coating system.

## EXPERIMENTAL

**Dedoping of Polyaniline.** Emeraldine salt, dodecylbenzenesulfonic acid (DBSA) doped polyaniline (PAni-DBSA), was dedoped using sodium ethoxide producing a blue emeraldine base. Emeraldine base was doped with either 1-hydroxyethylene-1,1-diphosphonic acid (HEDP), 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC), or amino tri-(methylene phosphonic acid) (AMTP). Green, doped polyaniline powders were obtained.

**Primer Formulae.** The series of doped polyanilines, labeled PAni-HEDP, PAni-PBTC, and PAni-ATMP were each used as a pigmentitious inhibitor in a increasing polyaniline concentration series in epoxy-polyamide primers. Formulae were developed at constant pigment volume concentration (PVC) with increasing fraction of doped polyaniline concentration (0 (talc only, no polyaniline control), 5, 10 and 20 polyaniline volume concentration) in liquid epoxy Epon<sup>®</sup> Resin 828. All millbases had a Hegman gauge of 7 (ASTM D-1210). Coatings were prepared by letdown of the mixed millbase with a polyamide curing agent. Table 1 shows the talc control formulation that was used to dilute a polyaniline concentrate millbase.

Primers were applied to untreated cold rolled steel (CRS) and to iron phosphated-CRS Q-Panels using a coiled wire (Gardner #40) application bar. Applied primers were dried at ambient conditions for one week. Edges of primed panels were sealed with 1 mil green electroplaters tape to prevent corrosion in the unprimed areas while exposed to neutral salt spray or prohesion. Scribed panels were scribed using a carbide tip pencil. Individual panels were identified with polyaniline concentration in PVC, dopant type, and the sample

number (XXDDDD##). Phosphated substrates were additionally designated by the letter P suffix.

**Electrochemical Evaluations of Primed Panels.** For electrochemical testing, panels were cut into 3" × 1.5" and taped using 2 mil green electroplaters tape. The exposed area for testing was 1 cm<sup>2</sup>. Potentiodynamic and EIS measurements of doped polyaniline-containing epoxy-polyamide primers were performed using an EG&G Instruments potentiostat/galvanostat model 283. A Schlumberger high frequency response analyzer, model SI 1255, was used to perform electrochemical impedance spectroscopy (EIS). Panels were electrochemically evaluated before and after neutral salt spray exposure.

Table 1. Talc Control Formulation

Millbase	Quantity, (kg)	Solid Vol. (L)
Epon <sup>®</sup> Resin 828	324	277
Solsperse solution 24000/Oxsol100	19	4
Methyl-n-propyl ketone	269	0
Aromatic 100 Fluid	25	0
ANCARE <sup>™</sup> 2364	40	36
BYK-410	4	2
Talc (Mistron 600)	355	127
Total Millbase	1036	446
Letdown		
Deft Catalyst 02-Y-40	269	186
Total Formulation Weight	1305	623
% Solid (w/w)	70.17	
PVC	20.0	

Panels tested prior to neutral salt exposure by EIS and DC polarization possessed a controlled defect, a 0.031" diameter drilled pit.<sup>5</sup> Panels tested after neutral salt spray exposure, however, did not have drill pits. The electrochemical cell consisted of a Hg/Hg<sub>2</sub>SO<sub>4</sub> reference electrode, a 50 mm × 50 mm 100 mesh platinum counter electrode, the primed sample as the working electrode and 5% (w/w) K<sub>2</sub>SO<sub>4</sub> in distilled water as the electrolyte.

## RESULTS AND DISCUSSION

**EIS of Primers.** Bode plots (Figure 2) of polyaniline coated panels tested prior to neutral salt exposure, as a function of polyaniline concentration, generally showed that panels of 5 PVC PAni primers provided a larger barrier than higher concentrations to corrosion regardless of dopant structure. Panels coated with 5 PVC PAni showed higher corrosion resistance ( $R_{cor}$ ) than higher polyaniline concentration coatings. Phosphating the CRS substrates did not appear to affect corrosion resistance. However, corrosion resistance of PAni-HEDP, PAni-PBTC, and PAni-ATMP primers significantly decreased after salt spray exposure.

**DC Polarization.** Most of the data obtained from DC polarization measurement prior to neutral salt exposure showed a decrease in corrosion current as a function of increasing applied potential, supporting the tendency to passivate and prevent corrosion (Figure 3). Some panels, however, showed resistor-like behavior, e.g., panel 20ATMP18 (20 PVC PAni, ATMP doped, sample # 18), not passivation, as current increased nearly linearly with increasing potential. Resistor-like behavior was mainly observed in high concentration, i.e., 20 PVC PAni, coatings suggesting that the layer is increasingly permeable to the diffusion of corrosion species.

Most panels tested by DC polarization after salt spray exposure did not retain any passivation activity as observed prior to salt spray. All post salt spray samples reverted to resistor-like behavior (Figure 4), where current increased linearly as a function of potential

that is indicative of active corrosion. Only the 5 PVC PANi-ATMP on phosphated-CRS substrates appeared to retain any passivity

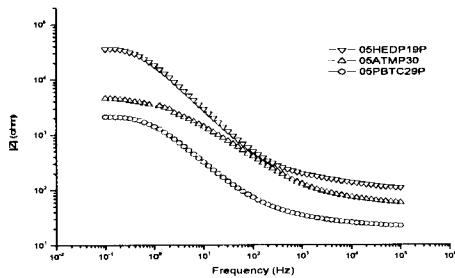


Figure 2. EIS for 5 PVC polyaniline coatings.

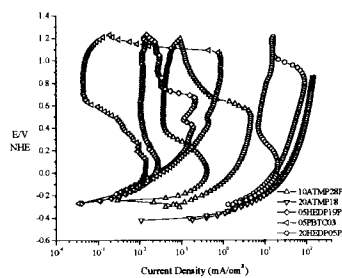


Figure 3. DC polarization for some polyaniline primers.

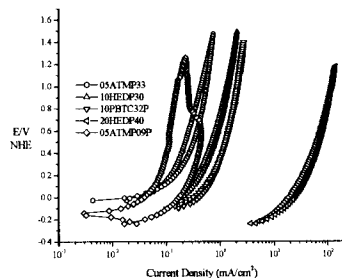


Figure 4. DC polarization curves for polyaniline coating after salt exposure.

**Corrosion Testing.** Accelerated corrosion testing by neutral salt fog exposure (ASTM B-117) of all polyaniline-primer systems, PANi-HEDP, PANi-PBTC, and PANi-ATMP epoxy-polyamide primers, was performed.

PAni-HEDP primers failed (ASTM D-1654 rating = 0) after 430 hr of salt spray exposure. Most panels had a #2 dense blistering (ASTM D-714) regardless of pretreatment of the panel or whether scribed. PANi-PBTC primers (rating 0, blister failure) failed after 500 hr of neutral salt fog exposure. Low scribe activity was observed, which could possibly be sacrificial. Most panels blistered at #2-4 dense regardless of pretreatment of the panel or whether scribed. PANi-ATMP primers showed the worst corrosion condition. PANi-ATMP systems, tested as scribed and unscribed panels, failed after 240 hr of salt exposure. Most panels gave blistering #6-8 medium dense, and a zero corrosion rating, regardless of pretreatment of the panel or whether scribed. All polyaniline primers of 20 PVC had a zero corrosion rating regardless of panel pretreatment, i.e., phosphating, or whether scribed. These results are interesting considering the lack of

corrosion (ASTM D-1654 = 10) observed by Kinlen, et al.,<sup>4</sup> which could be only ascribed to a different coating matrix.

All phosphonic acid doped, polyaniline inhibited primers failed by blistering, rather than a pinhole or scribe creep, mechanism(s). Osmotic blistering seems a reasonable explanation for the failure due to the hydrophilic nature of the phosphonic acid dopants. Adhesion was excellent before and after salt spray. The performance of the phosphonate doped polyanilines was worse than that reported for sulfonic acid doped polyaniline coatings.<sup>6,7</sup> Apparently, synergism with polyaniline did not occur.

The structure of dopants appear to play a role in the failure of the PANi-phosphonic acid primers based on our observations. An increase in the number of reactant polar groups per dopant molecule decreased the corrosion performance. The carboxyl groups of PBTC did not appear to affect corrosion resistance analogous to the phosphonate groups. Either the hydrophilic nature of the phosphonic acid dopants affected the performance of the coating, or alternatively the dopant level was too high that it catalyzed, rather than inhibited, corrosion.<sup>8</sup> For instance, lower PVC coatings containing less polyaniline and less phosphonate, performed better than higher PVCs.

Electrochemical testing gave evidence of corrosion inhibition by phosphonate doped polyaniline coatings as was reported in prior literature.<sup>4</sup> Nonetheless, neutral salt spray exposure showed opposite performance. Figure 5 displays doped polyaniline panels of 5 PVC after neutral salt spray exposure. Natural corrosion testing is underway.

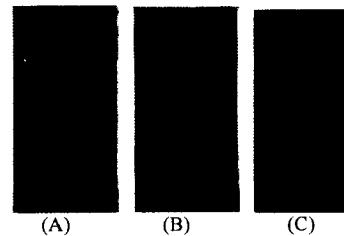


Figure 5. Dopant effect on corrosion inhibition in salt spray exposure, (a) 05ATMP33 after 240 hr, (b) 05HEDP37 after 430 hr, (c) 05PBTC after 500 hr.

## CONCLUSION

Post-electrochemical reflect performance obtained in neutral salt spray and show loss of corrosion passivity, despite retention of adhesion. Dopant structure and polarity appear to play a significant role in retention of barrier and electrochemical passivity.

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