

Inhibition of Corrosion-driven Coating Delamination on Zinc by Polyaniline Emeraldine salts

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Over the last decade a considerable body of research has been directed toward developing intrinsically conductive polymers as corrosion protective coating components. In this study dispersions of polyaniline emeraldine salt (PAni-ES) in a polyvinyl butyral (PVB) binder are shown to effectively inhibit corrosion-driven coating delamination (cathodic disbondment) from galvanized steel substrates in contact with aqueous chloride electrolyte. It is further shown that camphor-sulphonate (PAni-CSA) and phenyl phosphonate (PAni-PP) salts are significantly more efficient at reducing rates of cathodic disbondment than the commercially available *para*-toluenesulphonate (PAni-PTS) salt.

Each PAni-ES was prepared by dispersing polyaniline emeraldine base (PAni-EB) in a water/ethanol mixture containing an excess of the conjugate acid. The PAni-ES product was then repeatedly washed and filtered to remove free acid and dried in air. A solution of PVB was prepared in ethanol and any required amount of PAni-ES admixed by high-shear blending. The resulting dispersions were bar cast onto a galvanized steel surface to give a coating of $30 \pm 5 \mu\text{m}$ thickness containing a known volume fraction (ϕ) of PAni-ES. A penetrative coating defect was created in the coated substrate and corrosion driven coating disbondment initiated by introduction of 5% aqueous sodium chloride. Subsequently, in *in-situ* scanning Kelvin probe measurements were used to follow the kinetics of PVB/PAni-ES coating delamination over 48 hours at 20°C and 95% relative humidity.

Delamination of the PVB coating was detected by an irreversible drop in open circuit potential (E_{corr}). Thus the delamination front may be located from the E_{corr} inflection which propagates away from the coating defect in a wave-like fashion, as seen in fig 1a. Incorporation of PAni-ES was found to reduce the rate of delamination, as seen in fig 1b. Furthermore, with increasing ϕ a transition was observed from parabolic delamination kinetics (consistent with rate control by under-film cation migration) to linear kinetics (consistent with rate control by cathodic O_2 reduction). At sufficiently high ϕ all the PAni-ES's were capable of completely inhibiting coating delamination. However, inhibitor efficiency was found to increase in the order PAni-PTS < PAni-CSA < PAni-PP, as shown in fig 2.

It was found that oxidation of the zinc substrate by PAni-ES generates a zinc oxide layer at the coating-metal interface. We have used SIMS-depth profiling to demonstrate that oxide layer growth is complete within 6 hours of coating application and the thickness attained is proportional to ϕ^2 . Over a similar period of time the potential (E_{intact}) measured over the intact (undelaminated) PVB/PAni-PTS surface falls from a value approaching E^0 PAni-PTS (*ca* 0.4 V vs. SHE) to a value characteristic of PVB coated zinc (-0.25 ± 0.1 V vs. SHE). It is therefore proposed that inhibition arises principally as a result of the zinc oxide layer blocking cathodic O_2 reduction at the zinc-coating interface. It is further proposed that this effect is magnified and prolonged by the pH buffering action of residual in-coating PAni-PTS ($\text{p}K_{\text{a}}$ *ca* 5.5). That

is to say, PAni-PTS acts to absorb the OH^- ions produced by cathodic O_2 reduction and so prevents or delays alkaline dissolution of the zinc oxide barrier layer. The Pan-ES anions also influence the barrier integrity of the oxide layer and hence inhibitor efficiency.

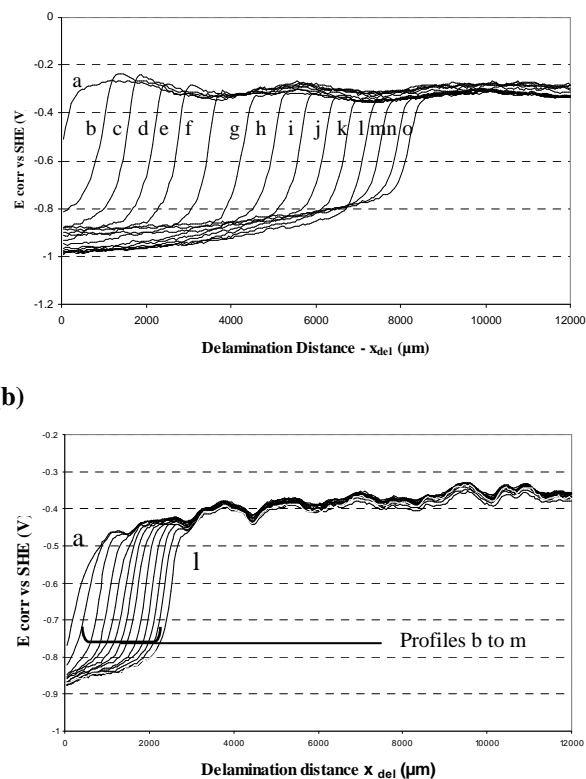


Fig 1 – Plots of time-dependent E_{corr} versus distance profiles recorded for a $30\mu\text{m}$ PVB coating on a galvanized steel, in the absence (a) and presence (b) of *p*Toluene sulphonate-exchanged Polyaniline pigment at ϕ 0.01. The electrolyte in contact with the defect is $0.86 \text{ mol dm}^{-3} \text{ NaCl (aq)}$. Time key: (a) curve a = 120min, b, c,...at 60min intervals from then on. (b) Curve a = 420min, b to l at 60min intervals thereafter.

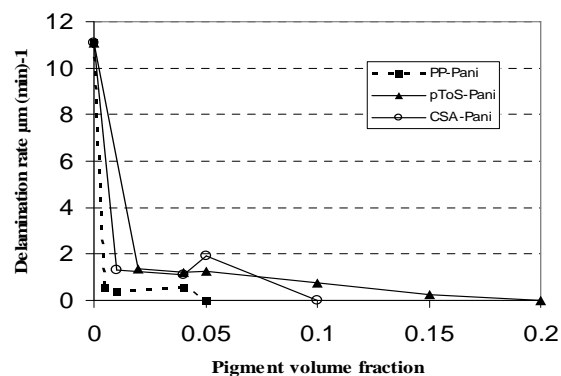


Fig 2 - Plots of delamination rate as a function of pigment volume fraction (ϕ) for PP-PAni., pTS-PAni and CSA-PAni.

References.

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2. G.Williams, R.J.Holness, D.A.Worsley, H.N.Mcmurray. Electrochemistry Communications 6 (2004) 549-555.