The inhibition of corrosion-driven organic coating delamination on iron by novel cation-exchange pigments studied using a scanning Kelvin probe

> G. Williams and H.N. McMurray Department of Materials Engineering University of Wales Swansea Singleton Park Swansea, SA2 8PP, U.K.

The well-documented toxicity and carcinogeneity of corrosion inhibitor pigments based on chromate salts has led to a considerable research effort to identify environmentally acceptable alternatives of equivalent efficiency. In this paper we describe how a low-cost, environment friendly, cation exchange pigment derived from naturally occurring bentonite clay may used to significantly enhance resistance to corrosion-driven delamination in organic coatings adherent to iron surfaces. A scanning Kelvin probe (SKP) is used to study the kinetics and mechanism of a corrosion-driven cathodic disbondment process affecting model poly-vinylbutyral (PVB)-based coatings adherent to polished iron substrates. The dependence of coating delamination rate on pigment volume fraction (ϕ) is determined for a range of cation exchanged bentonite pigments and compared with that of a conventional strontium chromate $(SrCrO_4)$ inhibitor.

The (Wyoming) bentonite clay is used both in its native form and exhaustively exchanged with a range of divalent alkali earth $(Mg^{2^+}, Ca^{2+}, Sr^{2+} and Ba^{2+})$ and trivalent rare earth $(Y^{3+} and Ce^{3+})$ metal cations. The native Wyoming bentonite is primarily sodium exchanged and is shown to be ineffective at slowing corrosion-driven delamination. All of the divalent and trivalent cation exchanged bentonites significantly retard the rate of delamination. However, the best inhibitor performance is achieved when the exchangeable cation is Ca^{2+} . A typical example is given in Fig 1, which shows the timedependent progress of a cathodic delamination front, marked by a region of sharp transition from high to low E_{corr} for a PVB coated iron surface in (a) the absence and (b) presence of Ca^{2+} -exchanged bentonite pigment. In absence of pigment the $E_{\rm corr}$ versus distance profile is characterized by a potential drop of 0.3-0.4V in the cathodic delamination zone. However, in the presence of Ca²⁺-exchanged bentonite pigment, markedly lower E_{corr} values are recorded in the delaminated region, suggesting an increase in cathodic polarisation

The effect of increasing Ca^{2+} -exchanged bentonite pigment volume fraction on the rate of corrosion-driven delamination is shown in Fig 2. For comparison, Fig 2 also shows the corresponding results obtained using SrCrO₄-pigmented PVB coatings. Although delamination is not completely halted in either case, similar reductions in rate are observed for Ca²⁺exchanged bentonite and SrCrO₄ at pigment volume fractions of 0.1 and higher.

Efforts to elucidate the mechanism by which the exchanged alkali earth and rare earth metal cations inhibit corrosion-driven delamination will be detailed. The effect of atmospheric carbon dioxide on the performance of the bentonite-based pigments is investigated to determine the importance of under-film carbonate film formation in the inhibition mechanism.



Figure 1: Plots of time-dependent E_{corr} versus distance profiles recorded for a 30 μ m PVB coating on a polished iron surface, in the absence (**a**) and presence (**b**) of Ca²⁺-exchanged bentonite pigment at $\phi = 0.15$. Electrolyte in contact with the defect is 0.86 mol dm⁻³ NaCl (aq). Time key: (a) curve a = 90min b,c... at 60min intervals thereafter, (b) curve a = 240min b,c... at 360min intervals thereafter.



Figure 2: Plots of delamination rate as a function of pigment volume fraction (ϕ) recorded for (**a**) Ca²⁺-exchanged bentonite and (**b**) SrCrO₄ pigments dispersed in PVB and coated on to polished iron substrates.