

Chromate mitigation in atmospheric corrosion by the use of smart-release pigments

H. Neil. McMurray and G. Williams
Materials Research Centre
Swansea University
Singleton Park
Swansea
SA2 8PP, UK

Despite concerted efforts over the last few decades, it is arguable that a credible, environmentally acceptable, equal for chromate-based inhibition of atmospheric corrosion (as it affects organic coated metals) has yet to be identified. This paper outlines an effective and immediately applicable approach for massively reducing the quantity of Cr(VI) used in a protective coating whilst retaining the full corrosion inhibition effect. The trick for doing this is to avoid using sparingly soluble chromate salts such as strontium chromate or zinc chromate and instead to store chromate ions in a water-insoluble smart-release pigment.

The advantages of such an approach are two-fold. Firstly the inhibitor is only released “on-demand”. For smart release pigments based on anion-exchange minerals (such as those to be described here) release is triggered only when aggressive anions such as chloride or hydroxide are encountered. In contrast a pigment comprising a sparingly soluble chromate salt (e.g strontium chromate) will continuously leach out chromate ions when in contact with an aqueous medium. Secondly, the smart-release pigment comprises a significantly lower chromate content per gram of solid. Whereas a strontium chromate (SrCrO_4) pigment has a CrO_4^{2-} content of 4.9 mmol g^{-1} , a chromate exchanged hydrotalcite pigment (HT-CrO_4^{2-}) comprises 0.35 mmol g^{-1} , representing a 15 fold decrease in Cr(VI) on a weight-for-weight basis.

In this paper a brief description is first given of the preparation of a HT-CrO_4^{2-} pigment and its incorporation into a model coating comprising polyvinylbutryal lacquer containing various volume fractions of pigment dispersion. Two types of atmospheric corrosion experiment are then described, in both of which the scanning Kelvin probe (SKP) is used to follow the rate of corrosion-driven coating failure (disbondment) and provide mechanistic information on inhibitor action. In the first type of experiment the cathodic disbondment of a PVB coating is followed on galvanized steel exposed to sodium chloride at 96%RH. In the second type of experiment filiform corrosion (FFC) is followed on PVB coated AA2024-T3 exposed to HCl at 93%RH.

Fig. 1 shows the effect of various in-coating volume fractions of HT-CrO_4^{2-} on the rate of corrosion-induced cathodic disbondment of a PVB coating on galvanized steel. For pigment volume fractions ≥ 0.1 delamination rates are reduced to a minimal level. It is shown that a similar performance is obtained for SrCrO_4 and HT-CrO_4^{2-} pigments incorporated at roughly comparable pigment volume fractions. It can be estimated that if a pigment volume fraction of 0.1 is used in each case, then the SrCrO_4 and HT-CrO_4^{2-} containing coatings comprises 1.9 and $0.07 \text{ mmol cm}^{-3}$ respectively (*i.e.* the HT-CrO_4^{2-} pigmented coating contains 27 times less chromate).

Fig. 2 shows the effect of incorporating 20% w/w SrCrO_4 and HT-CrO_4^{2-} pigments on the rate of FFC-induced coating disbondment on PVB coated AA2024-T3

It may be seen that to a similar extent, For both pigments the initial coating delamination rate is *ca.* $1.8 \times 10^{-3} \text{ mm}^2 \text{ min}^{-1}$, compared with $1.1 \times 10^{-2} \text{ mm}^2 \text{ min}^{-1}$ for the unpigmented case. However, as argued previously, the HT-CrO_4^{2-} pigment contains 15 times less available chromate than the same weight of SrCrO_4 .

On the basis of the above we can conclude that, the use of smart-release pigments can allow a massive reduction of chromate use without compromising protection against atmospheric corrosion.

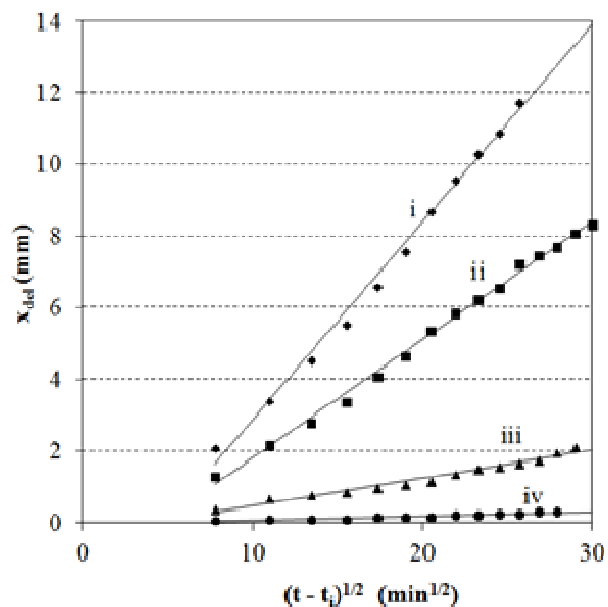


Fig. 1: Cathodic delamination distance (x_{del}) plotted as a function of $(t - t_i)^{1/2}$ for PVB coatings containing CrO_4^{2-} -HT pigment applied to HDG zinc substrates. Pigment volume fractions of (i) 0, (ii) 0.02, (iii) 0.05 and (iv) 0.1 were used, while the electrolyte in contact with a coating defect was 0.86 mol dm^{-3} aqueous NaCl.

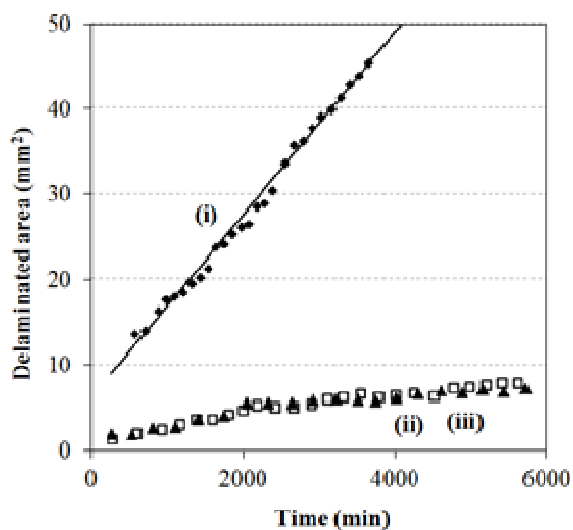


Fig. 2: FFC delaminated area, quantified by repetitive scanning of a fixed sample area by means of in-situ SKP, plotted as a function of time for PVB coated AA2024-T3 after exposing a coating defect to 0.5M HCl. Key: (i) unpigmented PVB, (ii) SrCrO_4 and (iii) HT-CrO_4^{2-} pigments at a coating loading of 20% w/w.

References.

1. G. Williams, H.N. McMurray, *Electrochem. Solid State Lett.*, 6, (2003), B9