Anti-Corrosion Smart Coatings Incorporating Hydrotalcite-Like Anion-Exchange Pigments

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Anti-corrosion coatings are described comprising novel, hydrotalcite-like, anion–exchange pigments dispersed in an organic polymer matrix. Hydrotalcite ($Mg_6Al_2(OH)_{16}CO_3.4H_2O$) and hydrotalcite (HT)-like compounds are known to act as effective halogen scavengers in polymer systems and as halide getters in aqueous solution.[1] Hydrotalcite and calcined hydrotalcites are also known to neutralise aqueous acids. Furthermore, HT-like coatings have been successfully used as anti-corrosion pre-treatments on aluminium.[2] Here we show how anti-corrosion pigments based on HT may be used to inhibit filiform corrosion (FFC) on AA2024-T3 aluminium alloy by neutralising filiform-head electrolyte pH and exchanging Cl^- for non-aggressive or corrosion-inhibiting anions. The coatings produced are smart in that inhibitor anions are only released when corrosive electrolyte is present.

HT exhibits a layer structure similar to brucite ($Mg(OH)_2$) but random substitution of Al^{3+} for Mg^{2+} in octahedral positions results in a positive layer charge balanced by carbonate anions in the interlayer space. HT-like compounds, are isomorphous with HT and may be represented by the general formula ($[Mg_{1-x}Al_x(OH)_2]^{x+}$ $[A^{n-}_{x/n}.yH_2O]$) where A^{n-} is an anion, and x lies in the range *ca.* 0.25-0.33. Upon heating to $450^oC – 800^oC$ HT loses CO_2 and water and transforms to a $MgO-Al_2O_3$ solid solution. However, when the solid solution is exposed to aqueous salt it re-hydrates and incorporates available anions to form new HT–like compounds.[3] It is this so-called *memory effect* which we have exploited to synthesise HT–pigments incorporating various anions including NO_3^-, CO_3^{2-} and CrO_4^{2-}.

The HT-pigments are dispersed (pigment volume fraction 0.2) in 30 μm polyvinyl butyral (PVB) coatings applied to the AA2024-T3 surface. Following FFC initiation by application of controlled amounts of dilute aqueous HCl to a penetrative coating defect the time-dependent extent of coating delamination is determined both optically and by means of repeated *in-situ* scanning using a scanning Kelvin probe (SKP) apparatus. All the HT-pigments are shown to profoundly reduce rates of coating delamination by comparison to un-pigmented samples. However, inhibitor efficiency is found to be dependent upon the exchangeable anion. It is also shown using SKP potentiometry that exchangeable chromate anions interact specifically with the metal surface to depress free corrosion potential values.

Fig. 1 shows delaminated area *vs.* time curves obtained using numerical integration of SKP potential distribution data for (a) unpigmented (b) HT-CO_3^{2-} (c) HT-NO_3^- and (d) HT-CrO_4^{2-} pigmented PVB coated samples. Curve (a) shows how the unpigmented coating delamination rate remains constant over the experimental period. However, curves (b)-(d), show that when HT-pigment is present inflections to markedly lower delamination rate are observable 1000 - 1500 minutes following FFC initiation. Fig. 2 shows the final (6000 min) FFC delaminated area obtained by optical image analysis. Again the extent to which the HT-pigments reduce FFC induced delamination varies with

KeyWords: Hydrotalcite, inhibitor, filiform corrosion

exchangeable anion and increases in the order $CO_3^{2-} < NO_3^- < CrO_4^{2-}$.

The above findings are rationalized by proposing that all the HT-pigments act to exchange aggressive Cl^- anions out of the electrolyte droplet present in the head of each advancing FFC filament and increase electrolyte pH through a acid-base and/or redox processes involving the anions exchanged in. It is further proposed on the basis of delamination rate and SKP potentiometry data that the exchangeable NO_3^- and CrO_4^{2-} anions act as inhibitors of the anodic and cathodic processes in FFC respectively.
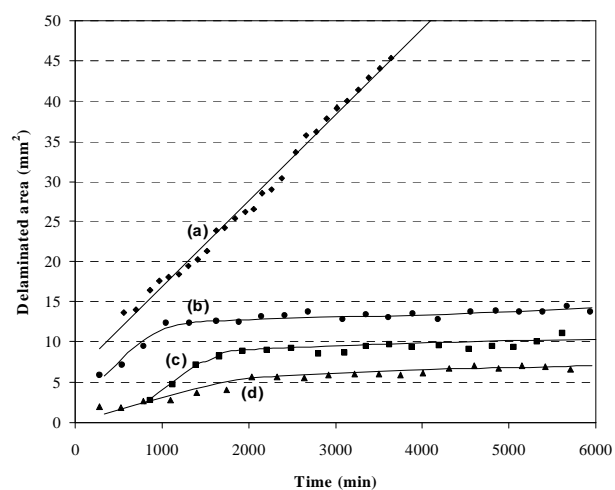

Figure 1 : FFC delaminated area, quantified by repetitive scanning of a fixed sample area by means of a SKP apparatus, plotted as a function of time for PVB coated AA2024-T3 samples in the presence and absence of HT inhibitor pigment. Key: **(a)** unpigmented PVB, **(b)** HT-CO_3^{2-}, (c) HT-NO_3^- and **(d)** HT-CrO_4^{2-}, all present at a pigment volume fraction of 0.2.
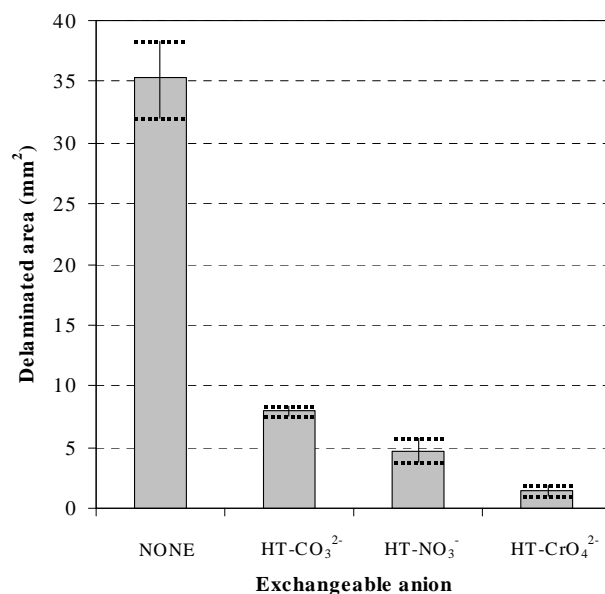

Figure 2: Delaminated sample area determined by optical image analysis of PVB coated AA2024-T3 samples 7 days following FFC initiation, obtained from the mean of 4 duplicate samples in each case.

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