

Correlation of Epoxy Adhesion to Hydrotalcite with Contact Angle and Electrokinetic Measurements.

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Introduction

Hydrotalcite (HT) conversion coatings are nonchromate coatings formed on aluminum alloys by immersion in alkaline lithium salt solutions. The macroscopic structure of HT coatings consists of blade-like crystals. The atomic structure of HT consists of oxoanions (such as nitrate or carbonate) intercalated between lithium-aluminum hydroxide layers.

The corrosion resistance of hydrotalcite (HT) conversion coatings has been optimized for standalone corrosion resistance^{1,2}. In practice, HT coatings will be used as part of a coating system consisting of a primer and one or more topcoats. Sufficient adhesion between HT conversion coatings and subsequent organic layers will factor into the corrosion performance of coating system with a HT conversion coating.

Adhesion results from mechanical and physico-chemical factors. Mechanical adhesion occurs by interlocking of the adhesive coating with surface asperities when sufficient wetting of the substrate has occurred. In the absence of complete wetting, voids at the interface compromise adhesion. It is believed that the blade-like HT morphology should provide good mechanical adhesion with subsequent layers, if the surface chemistry interactions are properly matched. In the present study, contact angle and electrokinetic measurements were employed to characterize the surface chemistry of HT coatings with different oxoanions. These results were correlated with practical adhesion tests for epoxy on HT coatings in the dry and wet state. Chromate conversion coatings (CCC) were used as a control.

Experimental Methods

The pull off tensile strength (POTS) was used as a parameter to gauge the practical adhesion of epoxy on HT conversion coatings. HT coatings were applied to AA2024-T3 substrates by bath immersion. Three HT chemistries (NO_3 , CO_3 , and $\text{NO}_3+\text{S}_2\text{O}_8$) were prepared. Epoxy coatings (BPA based resin + polyamide hardener) were spin cast onto the HT treated panels (25-75 μm thick). The POTS was measured according to ASTM D4541 for dry coatings and after 24 hours exposure to deionized water.

HT particles that precipitated in the bath during sample preparation were collected for contact angle and electrokinetic measurements. CCCs were applied to Al powder (ca. 20 μm) for the powder studies.

Contact angles were calculated using the rising height method. A liquid is allowed to wick through a cylinder of packed powder that is suspended from a microbalance. Washburn's equation was used to calculate the contact angle³. A series of well-characterized liquids (water, diiodomethane, formamide, and ethylene glycol) were used to calculate the surface tension. It has been proposed that the surface tension can be separated into Lifshitz-van der Waal (LW) and acid-base components such that the surface tension (γ) is expressed:

$$\gamma = \gamma_{\text{LW}} + 2(\gamma_+ \gamma_-)^{1/2}$$

where γ_+ and γ_- are the electron accepting and electron donating contributions to the acid-base component³. Combining the above equation with Young's equation, the surface tension of the powders can be calculated from

the contact angle data.

Electrophoresis was employed to measure the zeta potential (ζ) of the HT powders in 1mM KCl using the Helmholtz-Smoluchowski equation⁴. ζ was measured as a function of pH to determine the iso-electric point (IEP), the pH where ζ changes sign.

Results and Discussion

The POTS (wet and dry), surface tension components and IEP for the powders are listed in Table 1. The CCC had the highest POTS followed by the CO_3 HT for both the dry and wet state. The NO_3 HT had a higher POTS for the dry state than the $\text{NO}_3+\text{S}_2\text{O}_8$ HT. This was reversed in the wet state. In all cases the wet POTS was lower than that in the dry state as expected.

The dry state POTS was inversely related to the electron donicity parameter (γ_-) and to the IEP. The IEP of CCC was not measured in this study. However, the IEP of Al 1100 in 10 mM Cr(VI) has been reported as 8.2⁵. Assuming that CCC would have a similar surface chemistry, this result supports our observed trend. The IEP is indicative of relative basicity or acidity with high IEP indicating high basicity. It is not surprising that the conversion coatings with lower basicity (indicated by lower γ_- and IEP) have a higher dry state POTS with amine-cured epoxy, which is a basic material.

Interestingly, the parameter that correlated with the wet state POTS was γ^{LW} . In the presence of water, the acid-base interactions that control the dry state adhesion are disrupted. This is in agreement with earlier findings that wet state adhesion was highest on substrates with a high dispersive (LW) component⁶.

These results indicate that adhesion can be increased by modification of the HT surface chemistry. Current work is investigating the use of ionic surfactants to alter the interfacial properties.

Table 1. POTS (wet and dry), γ^{LW} , γ_- and IEP of HT powders with different interlayer oxoanion and CCC.

	POTS dry (psi)	POTS wet (psi)	γ^{LW} (mN/m)	γ_- (mN/m)	IEP
CCC	986	531	50.8	3.8	8.2 ⁵
CO3 HT	777	358	38.8	10.8	11.1
NO3 HT	722	320	24.1	19.6	11.3
NO3 + S2O8 HT	567	336	33.7	24.9	11.6

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