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Correlating Surface Roughness and Binder Erosion to Tint Retention of Coatings

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Tint retention, the ability to maintain the "as-painted" color appearance, is a critical property for exterior architectural coatings which are subjected to outdoor weathering conditions (notably UV irradiation and humidity and temperature cycles). A fundamental understanding of the phenomenon of tint retention is important to The Dow Coatings Materials business for product development. The Analytical Sciences group was involved to help identify the root cause for tint changes of exterior paints during simulated weathering tests and to evaluate how a coating additive affected tint retention.

The studies were conducted on two model paint formulations containing conventional acrylate-based binder and ≈15 PVC % TiO_2 particles, one with an additive and one without. Both formulations were weathered in the Q-Lab accelerated weathering tester (QUV) with UV and condensation cycles for various durations up to 2000 hrs. The analytical work consisted of tint measurement (X-Rite spectrophotometer), gloss measurement (BYK handheld gloss meter), roughness measurements by Atomic Force Microscopy (AFM) (Bruker Dimension Icon) and Optical Profilometry (OP, Wyko NT1000), surface composition analysis by X-ray Photoelectron Spectroscopy (XPS) (Thermo K-Alpha spectrometer) and Energy Dispersive X-ray Spectroscopy (EDS) (Thermo Scientific System Six), and surface morphology by Scanning Electron Microscopy (SEM) (FEI Nova NanoSEM 630).

The tint measurement was carried out using the "L*a*b*" color model, where the perceived color by human vision is described as a combination of the lightness (L*), which is strongly affected by gloss, and the red/green (a*) and yellow/blue (b*) color channels of the light coming from a given object. The coating without the additive showed a major change in the perceived color after brief weathering (<500 hours) (Figure 1a). The additive helped delay that process up to 1000 hours. The contribution of the pigment to the "true color" could be decoupled in the tint measurement and was found to undergo little change during the weathering test, suggesting no notable alteration had occurred to the pigmentation in the bulk of the coating. Separate gloss measurements revealed notable change in the gloss number over the course of the exposure (Figure 1b). The timing and extent of the gloss change also varied depending on whether the coating additive was added. The paint without the additive lost gloss initially but partially recovered the gloss after 1000 hours in the QUV. The additive was shown to help retain the initial gloss up to roughly 1500 hours of weathering before any major gloss loss took place.

The surface roughness profiles of the paint films were measured by AFM and OP as a function of weathering time. The roughness determined by AFM from 30 x 30 μm areas was found to give the best correlation to gloss as a function of weathering. The paint film without the additive showed a steeper onset of roughness at early time points (Figure 1c), but the trend reversed after 1000 hours in QUV. The film with the additive showed a flatter roughness increase at the beginning of the weathering test, but the rate eventually increased after 1500 hours. Elemental analysis of the weathered coating by SEM-EDS and XPS revealed an increased TiO_2 concentration, indicating that the binder was preferentially eroded

during weathering. The erosion rates estimated by XPS were similar but the rates by EDS within the top one micron of the coating film were qualitatively lower in the sample containing the additive. These observations were confirmed by SEM imaging acquired at a normal and at a grazing angle to the film surfaces (Figure 2a, b). By SEM, more TiO_2 particles could be seen protruding from the binder matrix with longer QUV exposure time. The samples with and without the coating additive had similar refractive indices and showed similar gloss and distributions of TiO_2 particles initially, but developed crucial differences over time. Without the additive, TiO_2 particles could be seen densely packed at the surface in the plan view. This suggests extensive binder loss had occurred resulting in several layers of the TiO_2 particles condensing and forming a packed layer. With the additive, the exposed TiO_2 was in more isolated clusters and less packed, indicating less binder erosion. In the grazing angle SEM images, the control samples appeared to be flatter at 2000 hours due to the densely packed TiO_2 layer. This may explain the partial reduction of roughness and increase of gloss towards the end of the experiment.

The accumulated results indicate that the root cause for the tint loss is the reduction in gloss due to the preferential erosion of binder, which in turn causes an increase in surface roughness and light scattering. The coating additive reduces the overall binder erosion rate and delays the gloss and tint loss.

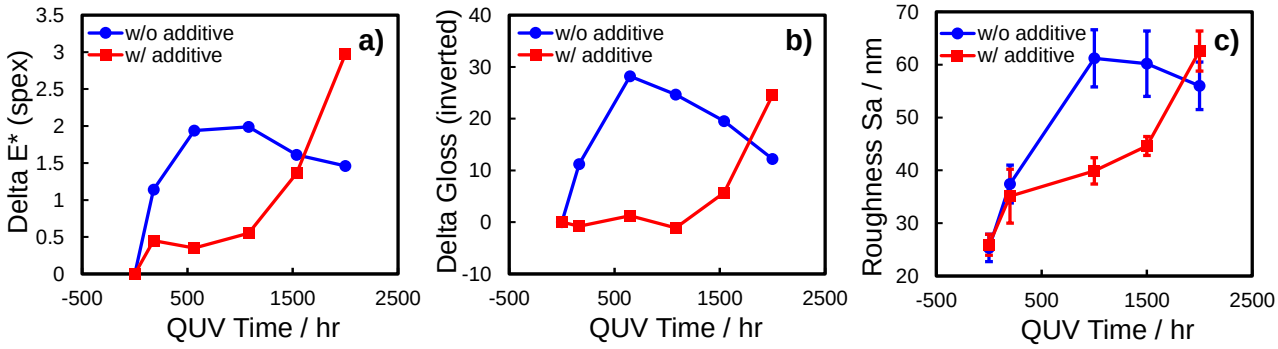

Figure 1. Change of a) tint, b) gloss (y axis inverted) and c) roughness of the coating films as a function of weathering time. The red and blue traces show the formulation w/ and w/o the additive, respectively.

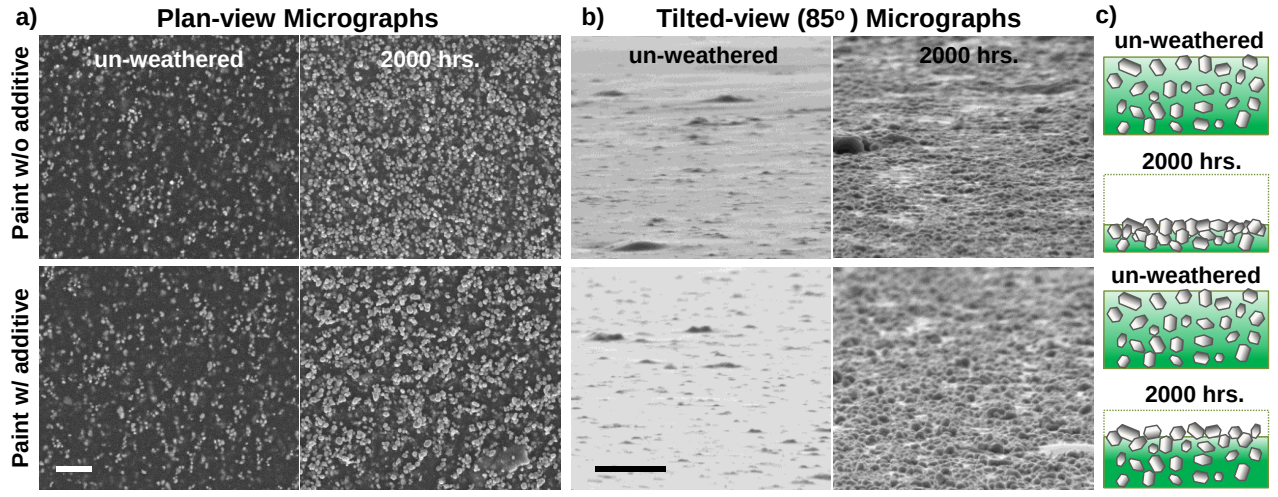

Figure 2. a) SEM plan view (5 keV landing energy) of paint surface, b) 85° tilted view (5 keV landing energy) and c) schematic depiction of the depth profile of TiO_2 distribution before and after weathering. The top and bottom rows show the formulation w/o and w/ the additive, respectively. Scale bar = 2 µm.

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