

# UC Berkeley

## UC Berkeley Previously Published Works

### Title

Stable Aqueous Dispersions of Hydrophobically Modified Titanium Dioxide Pigments through Polyanion Adsorption: Synthesis, Characterization, and Application in Coatings

### Permalink

<https://escholarship.org/uc/item/6743c1qd>

### Journal

Langmuir, 32(8)

### ISSN

0743-7463

### Authors

Janklovits, Joseph  
Kusoglu, Ahmet  
Weber, Adam Z  
[et al.](#)

### Publication Date

2016-03-01

### DOI

10.1021/acs.langmuir.5b03718

Peer reviewed

# Stable Aqueous Dispersions of Hydrophobically Modified Titanium Dioxide Pigments through Polyanion Adsorption: Synthesis, Characterization, and Application in Coatings

Joseph Jankolovits,<sup>†</sup> Ahmet Kusoglu,<sup>‡</sup> Adam Z. Weber,<sup>‡</sup> Antony Van Dyk,<sup>§</sup> James Bohling,<sup>§</sup> John A. Roper, III,<sup>||</sup> Clayton J. Radke,<sup>†</sup> and Alexander Katz<sup>\*,†</sup>

<sup>†</sup>Department of Chemical and Biomolecular Engineering, University of California, Berkeley 201 Gilman Hall, Berkeley, California 94720-1462, United States

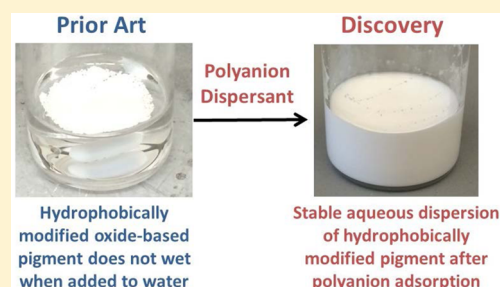
<sup>‡</sup>Energy Conversion Group, Lawrence Berkeley National Laboratory, MS 70-108B, 1 Cyclotron Rd., Berkeley, California 94720, United States

<sup>§</sup>The Dow Chemical Company, Collegeville, Pennsylvania 19426, United States

<sup>||</sup>The Dow Chemical Company, Midland, Michigan 48674, United States

## Supporting Information

**ABSTRACT:** Polyanion dispersants stabilize aqueous dispersions of hydrophilic (native) inorganic oxide particles, including pigments currently used in paints, which are used at an annual scale of 3 million metric tons. While obtaining stable aqueous dispersions of hydrophobically modified particles has been desired for the promise of improved film performance and water barrier properties, it has until now required either prohibitively complex polyanions, which represent a departure from conventional dispersants, or multistep syntheses based on hybrid-material constructs. Here, we demonstrate the aqueous dispersion of alkylsilane-capped inorganic oxide pigments with conventional polycarboxylate dispersants, such as carboxymethylcellulose (CMC) and polyacrylate, as well as a commercial anionic copolymer. Contact-angle measurements demonstrate that the hydrophobically modified pigments retain significant hydrophobic character even after adsorbing polyanion dispersants. CMC adsorption isotherms demonstrate 92% greater polyanion loading on trimethylsilyl modified hydrophobic particles relative to native oxide at pH 8. However, consistent with prior literature, hydrophobically modified silica particles adsorb polyanions very weakly under these conditions. These data suggest that Lewis acidic heteroatoms such as Al<sup>3+</sup> sites on the pigment surface are necessary for polyanion adsorption. The adsorbed polyanions increase the dispersion stability and zeta potential of the particles. Based on particle sedimentation under centrifugal force, the hydrophobically modified pigments possess greater dispersion stability with polyanions than the corresponding native hydroxylated particles. The polyanions also assist in the aqueous wetting of the hydrophobic particles, facilitating the transition from a dry powder into an aqueous dispersion of primary particles using less agitation than the native hydroxylated pigment. The application of aqueous dispersions of hydrophobically modified oxide particles to waterborne coatings leads to films that display lower water uptake at high relative humidities and greater hydrophilic stain resistances. This improved film performance with hydrophobically modified pigments is the result of better association between latex polymer and pigment in the dry film.



## INTRODUCTION

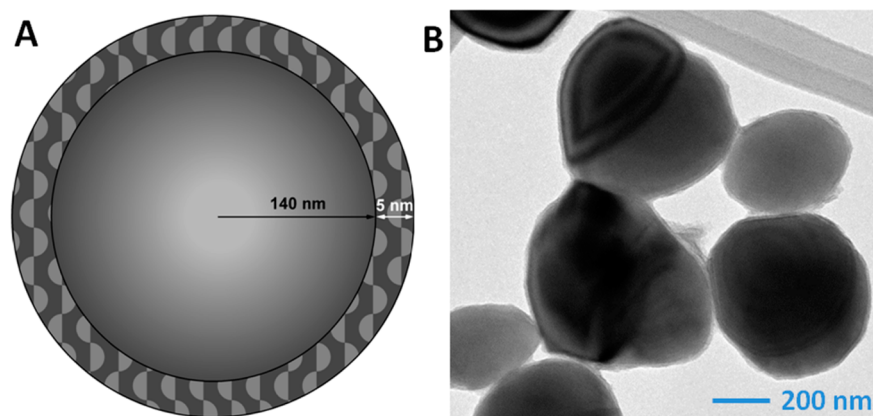
Inorganic oxide particles are used as pigments to provide opacity and color in many materials, such as architectural coatings. Controlling the dispersion of inorganic pigments is essential in paints because pigment aggregation decreases opacity, gloss, and barrier properties. Many commercial paint formulations use excesses of pigment to overcome the loss of opacity caused by pigment aggregation,<sup>1–4</sup> which contributes to titanium dioxide pigments alone accounting for 15 million metric tons of CO<sub>2</sub> emissions per year.<sup>5,6</sup> Poly(carboxylic acid)s possessing established polymer backbones (i.e., cellulose and acrylate) have emerged as essential technologies for minimizing pigment aggregation in applications such as waterborne paints and

coatings. Many literature studies have established that these polyanions adsorb on hydrophilic pigment surfaces, which leads to pigment dispersion through both steric and electrostatic stabilization.<sup>5,7–9</sup> However, to date, there has been no demonstration of dispersion of hydrophobically modified pigments using such polyanions, in a manner that retains hydrophobicity of the dispersed particle, and this represents a fundamental advance of this article. Indeed, in the past, attempts to disperse hydrophobically modified inorganic oxide particles, such as

**Received:** October 5, 2015

**Revised:** January 14, 2016

**Published:** January 20, 2016



**Figure 1.** (A) Schematic of the rutile  $\text{TiO}_2$  core and the  $\sim 5$  nm aluminosilicate shell on R706. (B) TEM micrograph of R706 particles.

organosilane-capped silica, with the same polyanions have uniformly failed.<sup>10,11</sup>

The ability to disperse hydrophobic pigment particles with conventional polyanion dispersants offers new opportunities in paints and coatings for improving performance. Poor association at the inorganic pigment–organic polymer interface is known to limit the mechanical and water-barrier properties of paint films.<sup>12,13</sup> Hydrophobic modification of inorganic oxide surfaces is a versatile approach to improving association at inorganic–organic interfaces.<sup>14</sup> For instance, hydrophobic chemisorbed monolayers can render glass water-repellent,<sup>15</sup> influence interfacial interactions in chromatographic separations,<sup>16,17</sup> and improve the adhesion of organic polymers to oxide surfaces.<sup>18,19</sup> The improved dispersion of hydrophobically modified oxide particles in hydrophobic organic–polymer films has been utilized in pigmented plastics<sup>20</sup> and bulk heterojunction solar cells.<sup>21</sup> Water penetration in porous solids is also inhibited by hydrophobic modification.<sup>22,23</sup> A long-term trend in coating materials has been the shift from organic to aqueous formulations to minimize the health and environmental impact of volatile organic compounds.<sup>24,25</sup> While hydrophobically modified pigments have many potential advantages for improving paint-film performance as discussed above, in the past, the challenge of wetting and dispersing these particles in water could only be overcome through elaborate synthetic modification of the polyanion or pigment surface. This has in turn limited the use of hydrophobically modified pigments in waterborne coatings.

This article uses unmodified polycarboxylates to obtain stable aqueous dispersions of hydrophobically modified titanium dioxide pigments. Commercial titanium dioxide pigments were hydrophobically modified with dimethylalkylsilane monolayers and dispersed using conventional unmodified polycarboxylates—the same ones that are used to disperse hydrophilic pigment particles and that failed to disperse hydrophobically modified inorganic oxide particles in the past (*vide supra*). We investigated carboxymethylcellulose adsorption and the contact angles on the hydrophobically modified particles to better understand the fundamental advance in hydrophobically modified particle dispersion using polyanions. We also demonstrate the preparation of waterborne paints possessing improved water-barrier properties and hydrophilic stain resistance using aqueous dispersions consisting of hydrophobically modified particles.

## EXPERIMENTAL SECTION

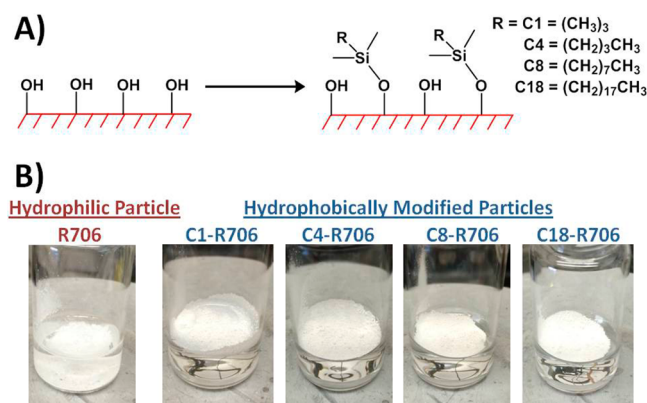
**Synthesis.** Ti-Pure R-706 (R706) was provided by DuPont. The particles are a rutile titanium dioxide pigment encapsulated by an  $\sim 5$  nm

aluminosilicate surface treatment that consist of on a weight basis, 93%  $\text{TiO}_2$ , 2.5%  $\text{Al}_2\text{O}_3$ , and 3%  $\text{SiO}_2$ ,<sup>26</sup> as shown in Figure 1 and Figure S1. Aluminosilicate surface treatments are commonly applied to titanium dioxide pigments to minimize their photoactivity and tune their dispersion behavior in water.<sup>20</sup> Under optimal dispersion conditions (0.25 mM pH 8 aqueous HEPES buffer), the hydrodynamic diameter of R706 as measured by dynamic light scattering on a Malvern Nano-Zetasizer was  $327 \pm 3$  nm. R706 possesses a low surface area of  $12.8 \text{ m}^2/\text{g}$  and modest internal microporosity that is localized in the aluminosilicate surface treatment.<sup>20</sup>

All other reagents were obtained from commercial sources. The polyanions investigated were sodium carboxymethylcellulose (NaCMC, MW = 90 000), sodium polyacrylate (MW = 15 000), and Tamol 1124, which is a commercial low molecular weight hydrophilic copolymer dispersant containing carboxylic acid groups.

Dynamic vapor sorption (DVS) measurements of the powders were carried out using a DVS analyzer with temperature and humidity control (Surface Measurement Systems, UK). The powders were placed into a glass sample pan and attached to the weight balance of the DVS. The samples were first dried at  $120^\circ\text{C}$  for 1 h to remove the moisture from the sample and determine its dry mass,  $M_0$ . The samples were then cooled down to  $25^\circ\text{C}$ , equilibrated for 30 min, and then humidified by holding it at 90% relative humidity (RH) for 6 h, followed by a dehumidification step back to 0% RH. The mass change in each sample due to vapor sorption/desorption,  $\Delta M$ , was recorded every second without any interruption between the steps. The change in the mass is normalized by the dry mass to calculate the percent mass change,  $\Delta M/M_0 \times 100$ . The sample pans were cleaned with acetone, IPA, and DI water and then air-dried before each experiment to eliminate any sample residue.

For the synthesis of the alkylsilane-capped pigment materials, the procedure is described below for R706 and in the Supporting Information for R931. R706 was washed once by suspending 100 g in 200 mL of water, isolating the solid by centrifuging the suspension and decanting the supernatant, and then air drying the solid. As illustrated in Figure 2A, a series of materials were prepared as described below with different dimethylalkylsilane monolayers, where the alkyl group on the dimethyl-substituted silane consisted of either methyl (C1-R706), butyl (C4-R706), octyl (C8-R706), or octadecyl group (C18-R706). Maximum hydrophobicity was achieved by performing the capping reaction on R706 that had been washed with water and air-dried at room temperature, which promotes a surface with a high density of native hydroxyl groups for maximum coverage of capping agents. These hydrophobically modified particles are resistant to aqueous wetting. The addition of 200 mg of the powder to 5 mL of water resulted in the solid resting on the surface of the liquid, as shown in Figure 2B. The C4-R706, C8-R706, and C18-R706 materials formed a more densely packed mass on the surface with a reduced surface area when contacting water. This qualitative observation is consistent with the hydrophobicity trends of alkylthiol monolayers on gold, which achieve maximum hydrophobicity with alkyl chains of five carbons or greater.<sup>27</sup> Surface-area



**Figure 2.** (A) Hydrophobic modification of an oxide surface by treatment with dimethylalkylchlorosilane reagents. Incomplete capping of the surface hydroxyl groups is expected due to the steric bulk of the silanes. (B) Highlight of the hydrophilic or hydrophobic surface chemistry of R706 and the alkylsilane-modified R706 materials, respectively. 200 mg of the powder was added to 5 mL of water. The hydroxyl-rich R706 readily penetrates the surface of the water while the alkylsilane-capped R706 materials do not wet spontaneously in water.

measurements were performed on a Micrometrics ASAP 2020 instrument. Samples were degassed at 110 °C, and nitrogen adsorption–desorption isotherms were measured at 77 K. As expected, the surface area of the particles decreased after alkylchlorosilane treatment because the capping groups limit access to internal micropores. The magnitude of this decrease was commensurate with the size of the silane (i.e. larger silane resulted in greater decrease).

**C1-R706.** In dry glassware under argon, 12 g of R706 was treated first with chlorotrimethylsilane (10 mL, Aldrich) followed by hexamethyldisilazane (15 mL, Aldrich). The suspension was sonicated for 1 min and stirred at 120 °C under reflux for 18 h. After cooling to room temperature, the solid was isolated by centrifugation (10 min at 14 000 rpm) and subsequently washed by redispersing via sonication and vortexing in 75 mL of acetone (twice), methanol (once), and water (twice). The solid was dried on a freeze-dryer and ground with a mortar and pestle, yielding a fine white powder that was resistant to wetting. Yield = 11.15 g. BET surface area = 11.0 m<sup>2</sup>/g.

**C4-R706.** This material was synthesized following the procedure for C1-R706 on a 4 g scale, substituting butyldimethylchlorosilane (10 mL, Aldrich) and anhydrous pyridine (1 mL, Aldrich). Yield = 3.6596 g. BET surface area = 9.0 m<sup>2</sup>/g.

**C8-R706.** This material was synthesized following the procedure for C1-R706 on a 12 g scale, substituting octyldimethylchlorosilane (25 mL, Aldrich) and anhydrous pyridine (2 mL, Aldrich). Yield = 11.5343 g. BET surface area = 9.1 m<sup>2</sup>/g.

**C18-R706.** This material was synthesized following the procedure for C1-R706 on a 12 g scale, substituting octyldodecylchlorosilane (4.1 g, Aldrich), anhydrous pyridine (2 mL, Aldrich), and toluene (25 mL). Yield = 11.76 g. BET surface area = 6.0 m<sup>2</sup>/g.

**SiO<sub>2</sub>.** Stöber silica particles were prepared based on literature precedent<sup>28</sup> via a modified procedure. Concentrated ammonium hydroxide (41.4 mL) was mixed with 532 mL of anhydrous ethanol under vigorous stirring. Tetraethoxy orthosilicate (120 mmol, 26.8 mL) was added, and the reaction was left to stir for 18 h. The solids were isolated by centrifugation at 14 000 rpm and washed in 75 mL of ethanol (four times) and water (twice) by redispersing via sonication and vortexing. The solid was dried on a freeze-dryer and ground with a mortar and pestle. Yield = 7.975 g. DLS average particle size = 226 ± 5 nm. BET surface area = 19.3 m<sup>2</sup>/g.

**C1-SiO<sub>2</sub>.** This material was synthesized by the procedure for C1-R706 on a 3.17 g scale. Yield = 2.94 g. DLS average particle size = 211 ± 3 nm. BET surface area = 17.1 m<sup>2</sup>/g.

**Electrokinetic Measurements.** Electrokinetic measurements were performed on a Malvern Nano-Zetasizer in a high-concentration zeta cell. All liquid solvents were filtered through a 0.2 μm syringe filter prior

to making dispersions. The electrokinetic pH profile of the particles was measured on 0.00023 vol % (0.01 mg/mL) suspension of the particles in 0.1 M aqueous sodium chloride. The pH was adjusted to the desired value with sodium hydroxide or hydrochloric acid. Samples were sonicated for 15 min prior to the zeta potential measurement.

For the change in the zeta potential with adsorbed CMC, aqueous 0.1 M NaCl solutions at pH 8 with 2.3 vol % solids were combined with varying amounts of CMC. These suspensions were diluted 100-fold with deionized water and dispersed by vortexing and sonication for at least 10 min. Each data point represents the average of at least four measurements.

**Dispersion Stability Measurements.** The dispersion stability of the particles was assessed by examining particle sedimentation under centrifugal force. The 0.025 vol % (1 mg/mL) suspensions of the R706 materials were prepared from stock solutions, dispersed by vortexing and sonication for 5 min in an Elmasonic S10-H sonicator, and then equilibrated by stirring for 18 h. After equilibration, the samples were sonicated for another 5 min. Dynamic light scattering verified the dispersion contained primary particles and not aggregates at this point. 1.3 mL of the stock solution was transferred to a 1.5 mL Eppendorf tube and centrifuged at 1500g for 90 s. 700 μL of the supernatant was carefully transferred to a cuvette. The light transmittance at 310 nm was measured on a SpectraMax M2 UV–vis absorption spectrometer.

**Carboxymethyl Cellulose Adsorption Isotherms.** Aqueous 1 wt % NaCMC stock solutions were prepared using either 1 M NaOH or HCl to adjust the pH to 5, 6.5, and 8. For R706 and TMS-R706 samples, 3.5 vol % (150 mg/mL) stock suspensions in deionized water were adjusted to the appropriate pH with 1 M NaOH or HCl to account for changes in the pH upon dilution. Samples with 1.5 mL total volume and 2.4 vol % solids were prepared by adding 1 mL of the stock suspension, 150 μL of 1 M NaCl, and the appropriate amounts of water and NaCMC stock solutions. The SiO<sub>2</sub> samples were weighed individually and prewet with ethanol (50 μL per 100 mg) and then mixed with 150 μL 1 M NaCl and the appropriate amount of water, 1 M NaOH or 1 M HCl, and CMC stock solutions to yield a 1.5 mL sample volume. The samples were thoroughly sonicated and vortexed to a homogeneous dispersion and then placed on a mechanical shaker overnight. The amount of adsorbed CMC was determined via a depletion method by quantifying the amount of residual CMC remaining in the liquid phase of the samples using the DuBois hydrolytic assay.<sup>29</sup> The supernatant of the sample after sedimenting the solid by centrifugation (298 μL); phenol (7 μL of an 80 wt % aqueous solution) and water (298 μL) were combined in a 2 mL vial, and concentrated sulfuric acid (745.5 μL) was carefully added. The vial was sealed, inverted three times to mix evenly, and placed on the benchtop. After 20 min, the visible absorption of the sample at 490 nm was measured on a SpectraMax M2 UV–vis absorption spectrometer. The amount of CMC in solution was then calculated by referencing a calibration curve.

**Capillary Rise Experiments.** The hydrophobicity of the particles was assessed through the capillary rise of aqueous solutions in packed beds of the materials. The 1.5 mm capillary tubes were plugged at one end with ~0.5 cm of packed cotton and then packed uniformly by (1) tapping the open end of the tube into the appropriate dry powdered material, (2) packing the column by inverting the tube and tapping the closed end on the benchtop, then further tamping the powder with a thin glass rod that fit inside the capillary, and (3) repeating steps 1 and 2 to reach a packed column height of 4 cm or greater. Care was taken to ensure consistent column packing with no observable voids in the material. The capillary was then immersed in an aqueous solution of 2.5 mM bromthymol blue at pH 8 such that only the cotton plug was below the surface of the liquid. Control experiments reveal the dye does not adsorb onto the R706 or C1-R706 surface. The capillary rise height was measured over time with a ruler. The liquid height in the solution continued to rise over 3 days of equilibration.

The height that water rises over time in a packed powder capillary ( $h$ ) is dependent on the contact angle of the solid ( $\theta$ ), as described by Washburn's equation (1) for the early stages of infiltration when gravity is negligible, where  $R$  is the capillary radius between particles,

$\eta$  is the solution viscosity,  $\gamma_{lv}$  is the liquid–vapor surface tension, and  $t$  is time.

$$h = \sqrt{\frac{R\gamma_{lv} \cos \theta}{2\eta}} \quad (1)$$

The contact angles of R706 samples with different surface modifications can be directly compared based on their capillary rise heights because  $R$  should not vary significantly between materials given the minor thickness of the alkylsilane monolayer and adsorbed polymer relative to the effective hydrodynamic radius between the particles. The relative hydrophobicity of the modified particles relative to R706 was related via their capillary rise height using a simple ratio derived from eq 1:

$$\frac{h_{\text{particle}}^2}{h_{\text{R706}}^2} = \frac{\cos \theta_{\text{particle}}}{\cos \theta_{\text{R706}}} \quad (2)$$

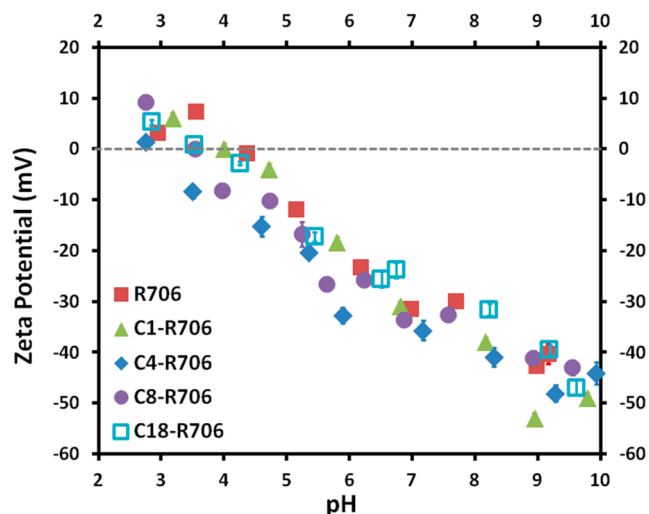
**Particle Redispersion.** The ease of obtaining a stable dispersion of hydrophobic particles in the presence of polyanions was assessed by examining sedimentation of the particles after providing minimal mechanical agitation to the suspension. 6–9 mg of solid was added to a 15 mL conical tube. The appropriate amounts of water, buffer, and polymer were gently added to provide a 0.025 vol % (1 mg/mL) particle suspension. The suspension was vortexed for 15 s, sonicated for 30 s, and shaken by hand. 1.3 mL of the stock solution was transferred to a 1.5 mL Eppendorf tube, which was centrifuged at 1500g for 90 s. 700  $\mu$ L of the supernatant was carefully transferred to a cuvette. The light transmittance at 310 nm was measured on a SpectraMax M2 UV–vis absorption spectrometer.

## RESULTS AND DISCUSSION

**Alkylsilane Monolayers on R706.** As a starting point for understanding polyanion adsorption and dispersion of hydrophobically modified pigments, we first consider the structure of the alkyldimethylsilane monolayers on the R706 surface. Extensive studies of capping oxides with trimethylsilane have shown that complete capping of all surface hydroxyl groups is impossible due to steric constraints. Amorphous silica has up to 4.6 hydroxyl groups/nm<sup>2</sup>,<sup>30</sup> while fully hydroxylated titania and alumina can possess even higher hydroxyl group densities.<sup>31,32</sup> Reliable estimates of trimethylsilane group coverage at the maximum packing density range from 1 to 2/nm<sup>2</sup>.<sup>2,33–36</sup> Therefore, uncapped surface hydroxyl groups should be present on materials with alkyldimethylsilane monolayers in water, even if the maximum surface coverage that is sterically possible was achieved.

None of the hydrophobically modified R706 materials wet spontaneously when added to water (Figure 2B), suggesting their contact angle is over 90°. Dynamic water vapor sorption analysis of C1-R706 shows no uptake of water from 90% relative humidity nitrogen gas, as shown in Figure 4. These data clearly demonstrate the hydrophobicity of C1-R706. In contrast, the native R706 material wets spontaneously and adsorbs water rapidly when humid nitrogen gas is passed over the dry powder. A 0.94% increase in mass is observed over 5 h on R706, which matches estimates for the amount of water needed to fill the micropores and saturate the surface of the particle.

To gain greater insight into the structure and surface chemistry of the dimethylalkylsilane monolayers on the R706 particles, the electrokinetic behavior was measured in water as a function of pH. R706 revealed an apparent isoelectric point (IEP) of pH 3.7 (Figure 3). Therefore, R706 possesses a negative surface charge in the pH 5–8 conditions utilized in this work. On mixed oxide surfaces, the IEP is influenced by the relative abundance of the different surface species. The IEP for R706 demonstrates that the surface is composed primarily of silica (IEP  $\sim$  2.5) and may



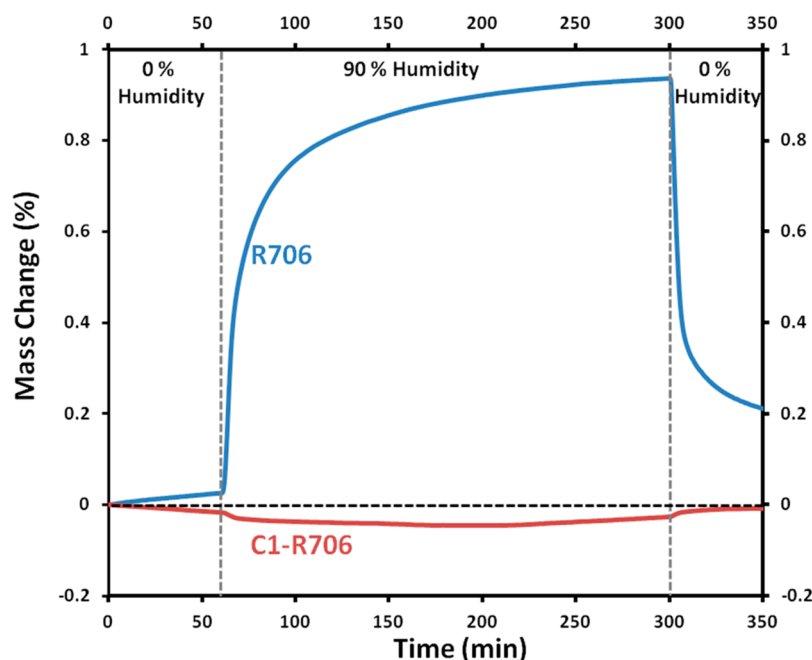
**Figure 3.** Plot of the zeta potential vs pH for unmodified and hydrophobically modified R706 materials in 0.1 mM NaCl.

have some smaller surface fraction that comprises alumina (IEP  $\sim$  7–9) and rutile titania (IEP  $\sim$  5.5).

Homogenous dispersions of the hydrophobically modified R706 particles were obtained in water with the aid of sonication. As shown in Figure 3, all of the hydrophobically modified powders exhibit the same electrokinetic profile and IEP of  $\sim$  3.7 as the unmodified R706 particles. Previous investigations on silica particles have also revealed identical electrokinetic pH profiles for hydroxylated and trimethylsilane-capped surfaces.<sup>37,38</sup> The hydrophobically modified particles acquire negative surface charge at elevated pH through the same mechanism as the unmodified oxide particles, namely the deprotonation of surface hydroxyl groups. The smaller number of surface hydroxyl groups and the hydrophobic environment around the remaining hydroxyls do not influence the zeta potential. These data are a consequence of incomplete hydroxyl group capping on the R706 particles during the dimethylalkylsilane treatments. Also, the electrokinetic profiles demonstrate the hydrophobically modified R706 particles to behave as charged interfaces in water.

**CMC Adsorption Isotherms.** Stabilizing particle dispersions using polyanions requires adsorption of the polymer on the particle surface. Once adsorbed, the polyanion provides electrostatic stabilization by increasing the net negative charge on the particle surface and steric stabilization from flexible loop and tail regions in the strand that extend from the particle surface.<sup>5,7–9</sup> The adsorption of a representative polyanion, carboxymethyl cellulose, was investigated on R706 and C1-R706 to establish the occurrence of the key pigment–polyanion interactions needed to form a stable dispersion. The DuBois assay was used to quantify CMC adsorption on the particle surface by the depletion of CMC from solution.<sup>29</sup>

Steep type 1 behavior is evident on R706 and C1-R706 at pH 5, 6.5, and 8, as shown in Figure 5. This strong adsorption is typical for a high molecular weight polymer like CMC (MW = 90 000 g/mol). The geometric footprint of a CMC monomer is roughly equivalent in size to the cellobiose monomer on poly(1  $\rightarrow$  4) $\beta$ -glucan, which has a footprint of 0.8 nm<sup>2</sup>.<sup>39,40</sup> For closely packed polymers via physisorption, monolayer coverage is achieved at 65% coverage, or 0.52 monomers/nm<sup>2</sup>.<sup>41</sup> At pH 5, R706 and C1-R706 display comparable adsorption behavior, with saturation coverages of 0.86  $\pm$  0.15 and



**Figure 4.** Dynamic vapor sorption data for R706 (blue) and C1-R706 (red) plotted as the change in mass of the dry powders vs time in a dynamic atmosphere that switches between 0% humidity dinitrogen and 90% humidity dinitrogen. The gray dashed line indicates a switch in the flowing gas.

$0.84 \pm 0.08$  monomers/nm<sup>2</sup>, respectively, corresponding to approximately 1.6 monolayers. This multilayer formation is presumably mediated by associated cations and substantial looping and tailing morphologies for the adsorbed CMC.<sup>42,43</sup>

The CMC loading decreases with increasing pH. At pH 6.5, saturation coverage on R706 and C1-R706 is  $0.37 \pm 0.05$  and  $0.44 \pm 0.07$  monomers/nm<sup>2</sup>, which is equivalent within experimental uncertainty. At pH 8, saturation coverage is  $0.13 \pm 0.02$  and  $0.25 \pm 0.04$  monomers/nm<sup>2</sup> for R706 and C1-R706, respectively. These data demonstrate higher adsorption capacities for the hydrophobically modified pigment at higher pH, when compared with the unmodified native oxide. Since the IEPs of both materials are  $\sim 3.7$ , the particles have a negative surface charge at the investigated pH's of 5, 6.5, and 8. CMC is also negatively charged under these conditions. Over 90% of the CMC carboxylates are deprotonated at pH 5, and complete deprotonation is achieved above pH 6.<sup>44</sup> CMC must therefore overcome electrostatic repulsion from the pigment surfaces for adsorption to occur. The greater CMC adsorption at lower pH can be rationalized on the basis of decreased electrostatic repulsion from fewer deprotonated hydroxyl groups on the particle surface.

Although perhaps counterintuitive from an electrostatic perspective, polyanion adsorption on negatively charged particles occurs on many oxide surfaces, including talc, hematite, titania, and alumina.<sup>45–51</sup> Polyanion loading also decreases in these systems as the pH increases relative to the IEP of the particle. In these systems, coordination of the polyanion to Lewis acid sites on the oxide is thought to facilitate polyanion adsorption. In particular, Al<sup>3+</sup> sites have been reported to significantly contribute to polyanion adsorption compared to Ti<sup>4+</sup> at high pH.<sup>52</sup> The release of anions from the double layer also promotes polyanion adsorption above the isoelectric point of the particle through entropic effects. The work of Boisvert et al. suggests that ion pairing interactions between the polyanions and M–OH<sub>2</sub><sup>+</sup> sites on the particle surface can also facilitate polyanion adsorption.<sup>52</sup>

Comparative CMC adsorption isotherms were also measured on Stöber silica (SiO<sub>2</sub>) and trimethylsilyl-capped Stöber silica (C1-SiO<sub>2</sub>) as controls. These materials possess isoelectric points of  $\sim 2.5$ , so they are also negatively charged in the investigated pH range, as is R706. The R706 surface is composed primarily of silica although some Lewis acidic Al<sup>3+</sup> sites are also present on the surface. Therefore, the SiO<sub>2</sub> and C1-SiO<sub>2</sub> particles provide insights into CMC adsorption in the absence of Al<sup>3+</sup> sites. Consistent with previous studies,<sup>10,11,53–55</sup> minimal CMC adsorption occurs on the SiO<sub>2</sub> and C1-SiO<sub>2</sub> particles, with less than 0.05 and 0.15 monomers/nm<sup>2</sup> at pH 8 and 5, respectively, even with large excesses of CMC in solution. The weak adsorption on silica greatly contrasts the high CMC coverage and affinity observed with R706 and C1-R706. These data demonstrate two key points on polyanion–pigment interactions. First, hydrophobicity alone is insufficient for strong polyanion adsorption given the electrostatic repulsion between the polyanion and particle surface. Hydrophobicity is instead a secondary factor in polyanion adsorption. Second, Al<sup>3+</sup> sites drive CMC adsorption on R706 and C1-R706 because almost no interaction is evident on silica, a surface that lacks such Lewis acidic functionalities. On the hydrophobically modified pigment, Lewis acidic sites on the inorganic surface underneath the alkyldimethylsilane monolayers drive polyanion adsorption. In summary, the silica controls above elucidate the crucial role of acidic sites, such as Al<sup>3+</sup>, in driving polyanion adsorption on hydrophobically modified oxide particles.

We envision two modes of polyanion interactions with hydrophobically modified particles. First, a carboxylate on the polyanion might interact directly with the Lewis acidic sites through coordination. For the Al<sup>3+</sup> sites to be accessible to a carboxylate on the polyanion, this model assumes patches of alkyldimethylsilane groups on the capped surface, which can result from the random irreversible attachment of the silanes. Alternatively, the carboxylate on the polyanion might interact with the surface via ion-pairing with protonated hydroxyl groups on Al<sup>3+</sup> surface sites. Boisvert et al. have demonstrated that

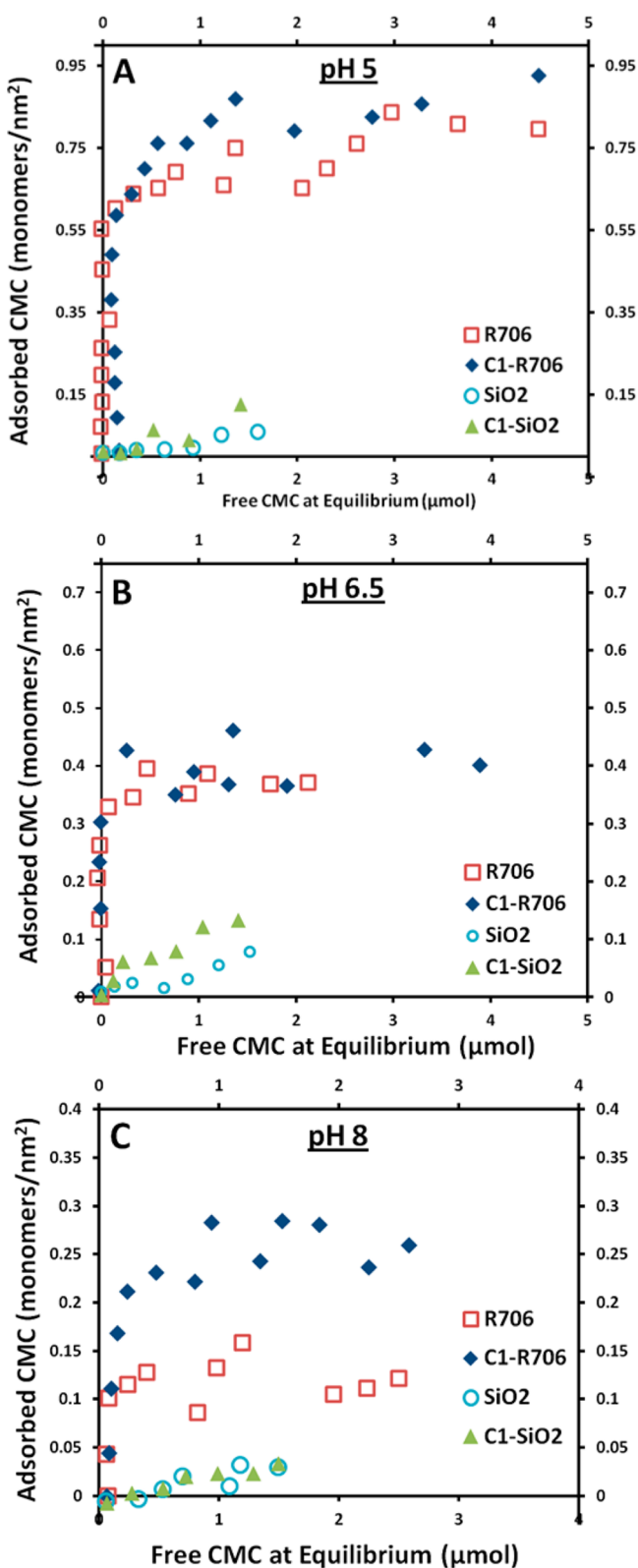


Figure 5. CMC adsorption isotherms on R706, C1-R706, SiO<sub>2</sub>, and C1-SiO<sub>2</sub> at pH (A) 5, (B) 6.5, and (C) 8 in 0.1 M NaCl.

positively charged surface sites persist on Al<sup>3+</sup> containing oxide particles at pH 9.<sup>52</sup> Therefore, protonated hydroxyl groups must also be considered as possible adsorption sites for polyanions on the hydrophobically modified R706 particles in the pH 5–8 range. For this ion-pairing model, one must consider that the steric bulk of the alkyltrimethylsilane monolayers must increase

the distance separating the paired ions relative to an uncapped surface. Since the alkylsilane monolayers constitute low dielectric media, the electrostatic attraction can remain high according to Coulomb's law. We believe that both mechanisms are feasible and a combination of coordination and ion pairing may occur in these systems. With either mechanism, we infer that fewer sites are present on the hydrophobically modified surface for polyanion attachment. Therefore, we expect the polyanions on the hydrophobically modified particles to possess a greater loop size.

At pH 8, the saturation CMC coverage on C1-R706 is almost 2 times greater than R706. We expect the higher loading is achieved because the hydrophobic effect<sup>56</sup> increases the affinity of the polyanion for the surface. Since C1-R706 is hydrophobic, the aqueous solvation shell should be weakly bound and possesses an entropically unfavorable ordered structure. CMC adsorption releases this water into bulk solution where it is less ordered, which is thermodynamically preferred. In contrast, the aqueous solvation shell around R706 will interact favorably with the surface hydroxyl groups and not suffer the same entropic penalty as a water layer on a hydrophobic surface. In support of this finding, hydrophobic surface modification has also been shown to increase the loading of polyvinylpyrrolidone on silica and polyacrylamide derivatives on gold surfaces.<sup>57,58</sup>

C1-R706 exhibits increased CMC loading at pH 8, but not at lower pH. We suspect this finding is a result of the low polyanion surface coverage at high pH. The CMC adsorption energy can be divided into components for electrostatic repulsion, attraction to the inorganic surface, and the hydrophobic contribution. At low pH, electrostatic repulsion is relatively low on both the hydrophobically modified and native R706 particles; therefore, the attraction to the inorganic surface can dominate the adsorption, leading to high coverage and little effect of hydrophobic capping. At high pH, electrostatic repulsion is greater. Therefore, the overall surface coverage is lower and the hydrophobic component can exert a greater influence on CMC loading.

CMC adsorption on R706 and C1-R706 causes a concomitant negative shift in the zeta potential of the particles, as shown in Figure 6. The zeta potential decreases sharply by over 30 mV under these conditions once the CMC saturation coverage is

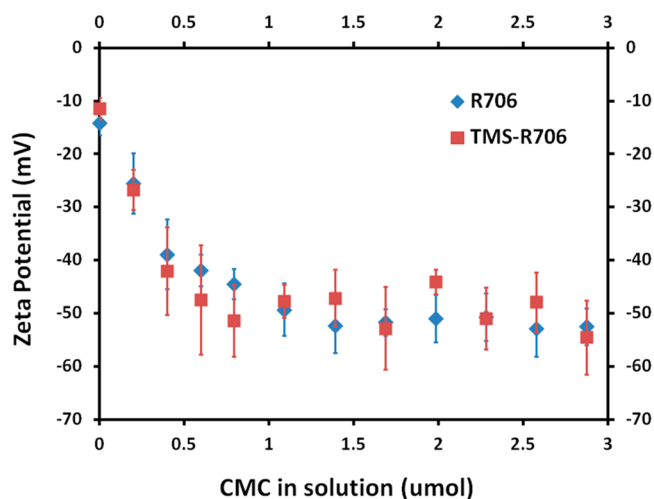
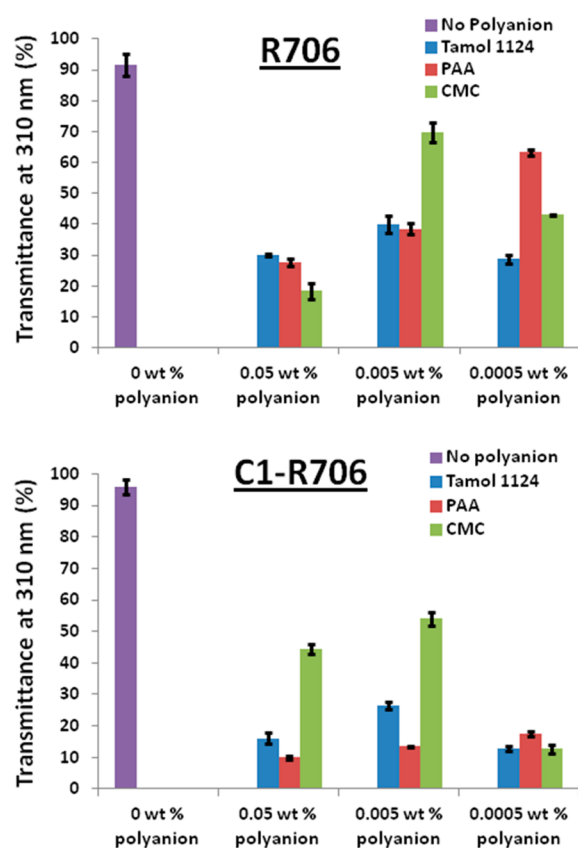


Figure 6. Change in the zeta potential of 100 mg/mL R706 and C1-R706 with added NaCMC in aqueous 0.1 M NaCl at pH 8. The samples were diluted 100-fold with deionized water for the measurements. The plot parallels the high CMC affinity measured in the adsorption isotherms.

reached (as predicted by the adsorption isotherms). Excesses of CMC do not influence the zeta potential of the particle. These data suggest that adsorbed polyanions provide electrostatic stabilization to dispersions of the pigments.

**Stable Aqueous Dispersions of Hydrophobically Modified Oxide Particles.** Polycarboxylates are common dispersants for paint pigments like R706.<sup>59</sup> Given the strong adsorption of CMC on C1-R706, the effect of polyanions on the dispersion stability of the hydrophobically modified R706 particles was investigated by examining particle sedimentation of dilute suspensions under centrifugal force. The effect of different polyanion types and concentrations on the dispersion stability of R706 and C1-R706 in 0.25 mM pH 8 HEPES buffer are displayed in Figure 7. Without any polyanion present, the



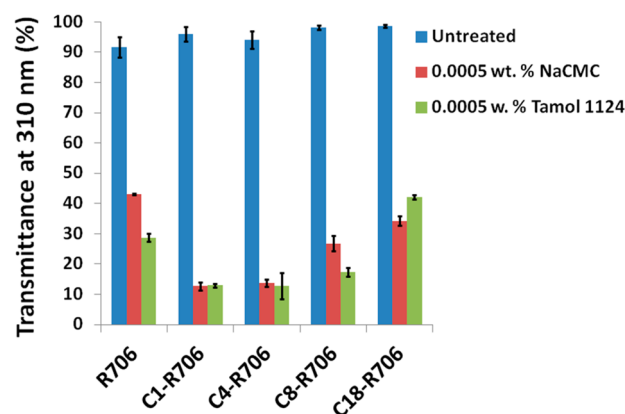
**Figure 7.** Effect of polyanions at different concentrations on the dispersion stability of 0.025% vol. suspensions of R706 and C1-R706 in 0.25 mM pH 8 aqueous HEPES buffer solutions based on the transmittance at 310 nm through the supernatant after centrifugation at 1500 g for 90 s. Based on the lower light transmittance, the polyanions decrease the sedimentation of the particles and improve the dispersion stability.

particles sediment readily, and the supernatant has high light transmittance. In the presence of polyanions, the stability of the particles is significantly enhanced as fewer particles sediment under the applied centrifugal force.

The data for C1-R706 indicate that a hydrophobically modified pigment can be dispersed by polyanions. In fact, the dispersion stability is greater for C1-R706 than the native R706 in most conditions. Improved dispersion stability was also observed in unbuffered water, which demonstrates that the HEPES buffer is not integral to the colloidal assembly (Figure S3). All three polyanions show comparable enhancements in the particle

dispersion stability at 0.0005 wt % polyanion. The stabilization is likely a result of greater surface charge and steric effects.<sup>5,7–9</sup>

The effect of different capping groups on the dispersion of hydrophobically modified oxide particles with polyanion dispersants was investigated. Figure 8 displays the effect of CMC



**Figure 8.** Effect of polyanions on the dispersion stability of unmodified and hydrophobically modified R706 materials based on the light transmittance at 310 nm of a 0.025 vol % suspension in 0.25 mM pH 8 HEPES buffer after centrifugation for 90 s at 1500 g.

and Tamol 1124 on R706 and the hydrophobically modified derivatives. In 0.25 mM pH 8 aqueous HEPES buffer, all particles exhibit improved dispersion stability with low concentrations of polyanions. C1-R706 and C4-R706 possess the greatest dispersion stability with both polyanions. Whitesides et al. have shown that on densely packed self-assembled monolayers a five-carbon chain is sufficient to mask underlying polar residues on the surface.<sup>15,60</sup> Since polyanions stabilize dispersions of C8-R706 and C18-R706, the polymer must interact with Lewis acidic sites on these surfaces. Therefore, we expect these monolayers are not densely packed. However, the lower dispersion stability of C8-R706 and C18-R706 compared to C1-R706 and C4-R706 (Figure 5) implies that the longer chains inhibit surface interactions to a limited extent. Nevertheless, these data demonstrate that stable aqueous dispersions of hydrophobically modified particles can be obtained with a variety of capping groups. The generality to other hydrophobically modified oxide particles is demonstrated with C1-R931 (Supporting Information). R931 is a commercial titanium dioxide pigment with a thicker aluminosilicate overlayer relative to R706. Using the conditions and analysis described above, C1-R931 dispersions are also stabilized by polyanions such as CMC and Tamol 1124 (Figure S4).

Homogenous suspensions of the C1-R706 and C4-R706 could also be obtained at higher concentrations of 19.8 vol % (49.7 wt %) solids (Table S2), which is more relevant to the higher pigment loadings of waterborne coating formulations, using a dual asymmetric centrifuge to disperse the particles, as described in the Supporting Information.

**Impact of Adsorbed Polyanions on Particle Hydrophobicity.** To understand how adsorbed polyanions influence the surface chemistry of the hydrophobically modified pigments, we investigated how adsorbed polyanions perturb the contact angle of C1-R706. Polyanion–particle composites were prepared by treating R706 and C1-R706 with CMC or Tamol 1124 and then briefly washing the materials with water to remove excess polyanion before isolating them as a dry powder (Supporting Information). These materials exhibited comparable dispersion stability to R706 and C1-R706 that were mixed *in situ*, confirming



**Table 1. Capillary Rise ( $h$ ) of 2.5 mM Bromthymol Blue Solution in 0.25 mM pH 8 Aqueous HEPES in Packed Columns of the Dry Powders after 225 min and the Estimated Contact Angle  $\theta$  Assuming the Value for R706 Is  $50^\circ$**

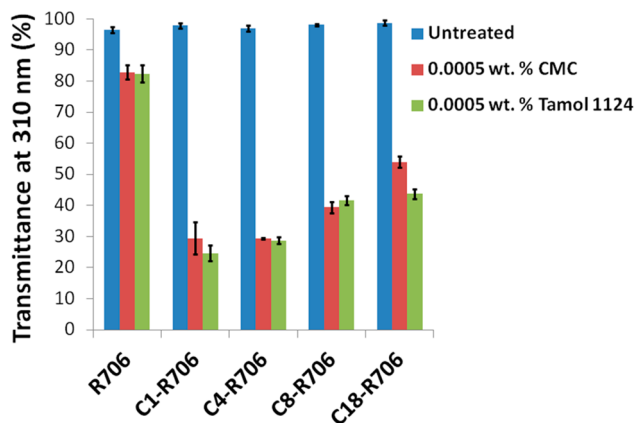
material	$h$ (cm)	$\theta$ (deg)
R706	$1.56 \pm 0.06$	50
R706-CMC	$1.81 \pm 0.02$	$29 \pm 6$
R706-Tamol 1124	$1.73 \pm 0.11$	$38 \pm 8$
C1-R706	$0.08 \pm 0.0303$	$>90$
C1-R706-CMC	$0.32 \pm 0.09$	$88 \pm 1$
C1-R706-Tamol 1124	$0.26 \pm 0.06$	$89 \pm 1$

the presence of the polyanion on the surface. The hydrophobicity was assessed through capillary rise experiments.<sup>61</sup> Dynamic rise heights for different materials are listed in Table 1. Water effectively does not rise in the C1-R706 capillary, which is consistent with it being a nonwetting material. Thus, the contact angle must be over  $90^\circ$ .

Greater capillary rise is observed in the R706–polyanion composites than with R706 (Table 1), demonstrating the adsorbed polyanions increase the hydrophilicity of the particles. Interestingly, the capillary rise for the C1-R706–polyanion composites is limited compared to the R706 materials. Greater capillary rise is observed for the C1-R706–polyanion composites than C1-R706, demonstrating that the adsorbed polyanions also make the pigment surface more hydrophilic, though the effect is modest. On the basis of these data, we hypothesized that the C1-R706 polyanion composites retain appreciable hydrophobic character. This is supported by the lack of water uptake during DVS measurements on C1-R706-CMC composites (see Figure S6).

The contact angles of the modified particles were estimated with eq 2 using a contact angle of  $50^\circ$  for R706, as displayed in Table 1. This value falls within the range measured for many  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{TiO}_2$  surfaces.<sup>62–64</sup> The contact angles for the C1-R706 composites with CMC and Tamol 1124 are greater than a typical oxide particle and substantially greater than the R706–polyanion composites. This relative hydrophobicity of the C1-R706 likely arises from the low surface coverage of the polyanion. The amount of CMC adsorbed on C1-R706 corresponds 0.25 monomers/ $\text{nm}^2$ , which corresponds to less than 50% of monolayer coverage at the jamming limit.<sup>41</sup> The magnitude of the change in the contact angle of R706 and C1-R706 particles after polyanion adsorption is consistent with literature examples. Beattie et al. found modest changes in the contact angle of hydrophobically modified silica upon the adsorption of polyacrylamide derivatives.<sup>58</sup> Bremmel et al. also found that the contact angle of talc decreased from  $82^\circ$  to  $65–75^\circ$  upon adsorbing different polysaccharides.<sup>65</sup>

**Dispersing Hydrophobically Modified R706 Particles in Water.** Wetting and dispersing pigments is a crucial stage in paint production that requires substantial mechanical agitation and dispersants to achieve a suspension of primary pigment particles.<sup>20</sup> We assessed how polyanions facilitate the dispersion of hydrophobically modified pigment particles in water. The minimum agitation for transitioning C1-R706 from a dry powder to a solution of dispersed particles at their primary particle size was identified in a 0.025 vol % suspension in 0.25 mM pH 8 HEPES buffer with 0.0018 wt % polyanion. Dynamic light scattering demonstrated that 15 s of vortexing followed by 30 s of sonication provided a dispersion of primary particles. Suspensions prepared via the minimum agitation conditions were then



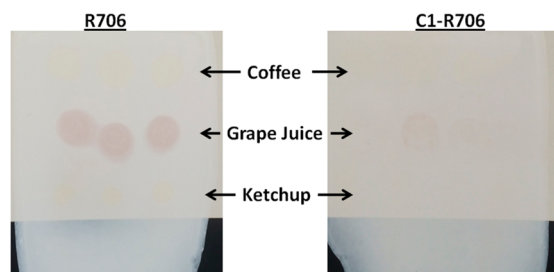
**Figure 9.** Effect of polyanions on the ease of redispersing untreated and hydrophobically modified R706 materials based on the light transmittance at 310 nm of a 0.025 vol % suspension in 0.25 mM pH 8 HEPES buffer prepared by the minimum agitation conditions of 15 s of vortexing and 30 s of sonication after centrifugation for 90 s at 1500 g.

centrifuged for 90 s at 1500 g to assess the state of the dispersion, and the light transmittance through the supernatant is shown in Figure 9. The hydrophobically modified particles exhibited limited settling under the centrifugal force with polyanions present. In contrast, the hydroxylated R706 material possessed poor dispersion stability.

We interpret these data as an indication that the polyanions facilitate the wetting and breaking apart of aggregates into primary particles. We suspect this effect is more pronounced on the hydrophobically modified R706 particles than the native R706 because of the higher polyanion affinity, as shown in Figure 5, and also faster polyanion adsorption on the alkyl-dimethylsilane monolayers than a hydroxylated surface. Recently, fast polymer adsorption on hydrophobic surfaces in water has also been observed for polysaccharides on graphitic carbon materials.<sup>66,67</sup>

**Impact of Hydrophobically Modified Pigments in Coatings.** We synthesized paint films using either R706 or C1-R706 pigment dispersions stabilized with Tamol 1124 dispersant and the same latex binder used in the adsorption experiments above (details of paint preparation are described in the Supporting Information). To assess the water barrier properties, free-standing films were cast at 13.8% pigment volume concentration (PVC, Table S3) by drying on release paper. Dynamic vapor sorption measurements on these films reveal substantially less water adsorbed in films formulated with C1-R706 than R706 at relative humidities above 40% (see Figure S6 and Table S5). For example, the paint with R706 undergoes a 3.7% weight increase at 90% relative humidity, while the increase with C1-R706 is only 2.9% (21.9% less than R706).

The water barrier properties were further assessed by examining the hydrophilic stain resistance of 22.9% PVC films that were cast using a latex applicator on laminated cards (see Experimental Section and Table S4). Three conventional hydrophilic stains consisting of coffee, grape juice, and ketchup were applied to the films for 30 min and carefully removed with a damp tissue. As shown in Figure 10, significantly less staining is evident in the films comprising the hydrophobically modified C1-R706 relative to unmodified R706. These DVS and hydrophilic stain test data reveal that formulating paints with polyanion stabilized dispersions of hydrophobically modified pigments can result in film coatings with improved water barrier and staining properties. These characteristics are consistent with



**Figure 10.** Stain testing results displaying 22.9% pigment volume concentration (PVC) paint films after applying stains for 30 min. The right panel comprising hydrophobically modified pigment contains significantly less staining compared with the left panel consisting of unmodified native-oxide pigment.

better association between latex polymer and pigment in the dry paint film, when the pigment surface is hydrophobically modified rather than a native oxide.

## CONCLUSIONS

The challenge of wetting and dispersing hydrophobically modified inorganic oxide particles in water with conventional polycarboxylate dispersants in a manner that retains hydrophobicity has until now prevented the use of hydrophobic pigment in waterborne coatings. To the best of our knowledge, this article presents the first stable aqueous dispersions of hydrophobically modified oxide particles using conventional, unmodified carboxylate-based polyanion dispersants. Using CMC adsorption isotherms, we demonstrated that polyanion adsorption on the hydrophobically modified pigments critically depends on the presence of Lewis acidic (such as  $Al^{3+}$ ) sites on the particle surface beneath the alkylsilane monolayer. The low surface coverage of polyanion on the pigment surface causes the particle to retain substantial hydrophobic character when dispersed in water. This in turn rationalizes the high water contact angles for the hydrophobically modified pigment particles, even with adsorbed polyanions. With polyanion dispersants, hydrophobically modified pigments possess aqueous dispersion stability that is equal to or exceeds that of the native-oxide particle. Advantageously, paint films synthesized with hydrophobically modified pigments adsorb less water and display improved hydrophilic stain resistance relative to films consisting of native-oxide particles. The latter two characteristics can be attributed to improved association at the pigment–binder (polymer) interface in the dry film, upon hydrophobic modification of the pigment surface.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.langmuir.5b03718.

Figures S1–S6 and Tables S1–S5 (PDF)

## AUTHOR INFORMATION

### Corresponding Author

\*E-mail askatz@berkeley.edu (A.K.).

### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

A.K. and A.Z.W. acknowledge support from the Assistant Secretary for Energy Efficiency and Renewable Energy, Fuel

Cell Technologies Office, of the U.S. Department of Energy under Contract DE-AC02-05CH11231. The authors are grateful to the Dow Chemical Company for support of this work.

## REFERENCES

- (1) F. B. Steig, J. The Effect of Extenders on the Hiding Power of Titanium Pigments. *Official Digest* **1959**, *31*, 52–64.
- (2) Ingham, B.; Dickie, S.; Nanjo, H.; Toney, M. F. In situ USAXS measurements of titania colloidal paint films during the drying process. *J. Colloid Interface Sci.* **2009**, *336*, 612–5.
- (3) Tiarks, F.; et al. Effects on the Pigment Distribution in Paint Formulation. *Macromol. Symp.* **2002**, *187*, 739–751.
- (4) Trapani, A.; Bleuzen, M.; Kheradmand, J.; Koller, A. The use of  $TiO_2$ -polymer composites to lower the environmental impact and improve performance of waterborne paints. *Farby I Lakieri* **2013**, *8*–18.
- (5) Farrokhpay, S. A review of polymeric dispersant stabilisation of titania pigment. *Adv. Colloid Interface Sci.* **2009**, *151*, 24–32.
- (6) Bedinger, G. M. U.S. Geological Survey, 2013.
- (7) Tadros, T. F. *Dispersion of Powders in Liquids and Stabilization of Suspensions*; Wiley-VCH Verlag GmbH & Co.: Weinheim, 2012.
- (8) Heller, W. Effects of Macromolecular Compounds in Disperse Systems. *Pure Appl. Chem.* **1966**, *12*, 249–274.
- (9) Vincent, B. The Effect of Adsorbed Polymers on Dispersion Stability. *Adv. Colloid Interface Sci.* **1974**, *4*, 193–277.
- (10) Poncet, C.; Tiberg, F.; Audebert, R. Ellipsometric Study of the Adsorption of Hydrophobically Modified Polyacrylates at Hydrophobic Surfaces. *Langmuir* **1998**, *14*, 1697–1704.
- (11) Poncet-Legrand, C.; Lafuma, F.; Audebert, R. Rheological behavior of colloidal dispersions of hydrophobic particles stabilised in water by amphiphilic polyelectrolytes. *Colloids Surf., A* **1999**, *152*, 251–261.
- (12) Kirsch, S.; et al. Scrub resistance of highly pigmented paints: A study on abrasion mechanisms of different scrub techniques. *Prog. Org. Coat.* **2001**, *43*, 99–110.
- (13) Thomas, N. L. The barrier properties of paint coatings. *Prog. Org. Coat.* **1991**, *19*, 101–121.
- (14) Ulman, A. Formation and Structure of Self-Assembled Monolayers. *Chem. Rev.* **1996**, *96*, 1533–1554.
- (15) Wasserman, S. R.; Tao, Y.-T.; Whitesides, G. M. Structure and Reactivity of Alkylsiloxane Monolayers Formed by Reaction of Alkyltrichlorosilanes on Silicon Substrates. *Langmuir* **1989**, *5*, 1074–1087.
- (16) Unger, K. K.; Becker, N.; Roumeliotis, P. Recent Developments in the Evaluation of Chemically Bonded Silica Packings for Liquid Chromatography. *J. Chromatogr.* **1976**, *125*, 115–127.
- (17) Kirkland, J. J. Development of some stationary phases for reversed-phase HPLC. *J. Chromatogr. A* **2004**, *1060*, 9–21.
- (18) Dvir, H.; Gottlieb, M. In *Bulletin of the American Physical Society*, Denver, CO, 2007.
- (19) Ramrus, D. A.; Berg, J. C. Using heterogeneous silane patterns to maintain adhesion and decrease water penetration into epoxy/aluminum interfaces. *J. Adhes. Sci. Technol.* **2006**, *20*, 1615–1623.
- (20) Braun, J. H.; Baidins, A.; Marganski, R. E.  $TiO_2$  pigment technology: a review. *Prog. Org. Coat.* **1992**, *20*, 105–138.
- (21) Bouclé, J.; Ackermann, J. Solid-state dye-sensitized and bulk heterojunction solar cells using  $TiO_2$  and  $ZnO$  nanostructures: recent progress and new concepts at the borderline. *Polym. Int.* **2012**, *61*, 355–373.
- (22) Fadeev, A. Y.; Eroshenko, V. A. Study of Penetration of Water into Hydrophobized Porous Silicas. *J. Colloid Interface Sci.* **1997**, *187*, 275–282.
- (23) Checco, A.; Hofmann, T.; DiMasi, E.; Black, C. T.; Ocko, B. M. Morphology of air nanobubbles trapped at hydrophobic nanopatterned surfaces. *Nano Lett.* **2010**, *10*, 1354–8.
- (24) Wicks, Z. W.; Jones, F. N.; Pappas, S. P.; Wicks, D. A. *Organic Coatings: Science and Technology*, 3rd ed.; John Wiley & Sons, Inc.: Hoboken, NJ, 2007.

- (25) Keddie, J. L. Film formation of latex. *Mater. Sci. Eng., R* **1997**, *21*, 101–170.
- (26) Dupont, 2007.
- (27) Bain, C. D.; et al. Formation of Monolayer Films by the Spontaneous Assembly of Organic Thiols from Solution onto Gold. *J. Am. Chem. Soc.* **1989**, *111*, 321–335.
- (28) Stober, W.; Fink, A. Controlled Growth of Monodisperse Silica Spheres in the Micron Size Range. *J. Colloid Interface Sci.* **1968**, *26*, 62–69.
- (29) Dubois, M.; Gilles, K. A.; Hamilton, J. K.; Rebers, P. A.; Smith, F. Colorimetric Method for Determination of Sugars and Related Substances. *Anal. Chem.* **1956**, *28*, 350–356.
- (30) Zhuravlev, L. T. The surface chemistry of amorphous silica. Zhuravlev model. *Colloids Surf., A* **2000**, *173*, 1–38.
- (31) Gazit, O. M.; Katz, A. Understanding the role of defect sites in glucan hydrolysis on surfaces. *J. Am. Chem. Soc.* **2013**, *135*, 4398–402.
- (32) Lusvardi, V. S.; Barteau, M. A.; Dolinger, W. R.; Farneth, W. E. Influence of Surface Hydroxyls on the Adsorption and Reaction of Ethanol on Polycrystalline Titania. *J. Phys. Chem.* **1996**, *100*, 18183–18191.
- (33) Finklea, H. O.; Vithanage, R. Infrared Absorption Spectroscopy of Chemically Modified Titanium Dioxide. *J. Phys. Chem.* **1982**, *86*, 3621–3626.
- (34) Evans, B.; White, T. E. Adsorption and Reaction of Methylchlorosilanes at an Aerosil Surface. *J. Catal.* **1968**, *11*, 336–341.
- (35) J. Duchet, B. C.; Chapel, J. P.; Gerard, J. F.; Chovelon, J. M.; Jaffrezic-Renault, N. Influence of the Deposition Process on the Structure of Grafted Alkylsilane Layers. *Langmuir* **1997**, *13*, 2271–2278.
- (36) Duchet, J.; Gerard, J.-F.; Chapel, J.-P.; Chabert, B. Grafting of alkylchlorosilanes onto silica from solution for adhesion enhancement. *J. Adhes. Sci. Technol.* **2000**, *14*, 691–718.
- (37) Eakins, W. J. Silanol Groups on Silica and Their Reactions with Trimethyl Chlorosilane and Trimethylsilanol. *Ind. Eng. Chem. Prod. Res. Dev.* **1968**, *7*, 39–43.
- (38) Laskowski, J.; Kitchener, J. A. The Hydrophilic-Hydrophobic Transition on Silica. *J. Colloid Interface Sci.* **1969**, *29*, 670–679.
- (39) Sullivan, A. C. Cellulose: the structure slowly unravels. *Cellulose* **1997**, *4*, 173–207.
- (40) Jankolovits, J. Single-Pot Encapsulation of Oxide Particles within a Polysaccharide Multilayer Nanocoating. *Adv. Mater. Interfaces* **2015**, *2*.
- (41) Wang, J.-S.; Pandey, R. B. Kinetics and Jamming Coverage in a Random Sequential Adsorption of Polymer Chains. *Phys. Rev. Lett.* **1996**, *77*, 1773–1776.
- (42) Sun, J.; Bergstrom, L.; Gao, L. Effect of Magnesium Ions on the Adsorption of Poly(acrylic acid) onto Alumina. *J. Am. Ceram. Soc.* **2001**, *84*, 2710–2712.
- (43) O'Shaughnessy, B.; Vavylonis, D. Irreversible adsorption from dilute polymer solutions. *Eur. Phys. J. E: Soft Matter Biol. Phys.* **2003**, *11*, 213–30.
- (44) Cuba-Chiem, L. T.; Huynh, L.; Ralston, J.; Beattie, D. A. In Situ Particle Film ATR FTIR Spectroscopy of Carboxymethyl Cellulose Adsorption on Talc: Binding Mechanism, pH Effects, and Adsorption Kinetics. *Langmuir* **2008**, *24*, 8036–8044.
- (45) Wang, J.; Somasundaran, P. Adsorption and conformation of carboxymethyl cellulose at solid-liquid interfaces using spectroscopic, AFM and allied techniques. *J. Colloid Interface Sci.* **2005**, *291*, 75–83.
- (46) Foissy, A.; Attar, A. E.; Lamarche, J. M. Adsorption of Polyacrylic Acid on Titanium Dioxide. *J. Colloid Interface Sci.* **1983**, *96*, 275–287.
- (47) Bhosale, P. S.; Chun, J.; Berg, J. C. Electrophoretic mobility of poly(acrylic acid)-coated alumina particles. *J. Colloid Interface Sci.* **2011**, *358*, 123–8.
- (48) Nsib, F.; Ayed, N.; Chevalier, Y. Comparative study of the dispersion of three oxide pigments with sodium polymethacrylate dispersants in alkaline medium. *Prog. Org. Coat.* **2007**, *60*, 267–280.
- (49) Kirwan, L. J.; Fawell, P. D.; van Bronswijk, W. An in Situ FTIR-ATR Study of Polyacrylate Adsorption onto Hematite at High pH and High Ionic Strength. *Langmuir* **2004**, *20*, 4093–4100.
- (50) Phenrat, T.; et al. Stabilization of aqueous nanoscale zerovalent iron dispersions by anionic polyelectrolytes: adsorbed anionic polyelectrolyte layer properties and their effect on aggregation and sedimentation. *J. Nanopart. Res.* **2008**, *10*, 795–814.
- (51) Sommerauer, A.; Sussman, D. L.; Stumm, W. The Role of Complex Formation in the Flocculation of Negatively Charged Sols with Anionic Polyelectrolytes. *Colloid Polym. Sci.* **1968**, *225*, 147–154.
- (52) Boisvert, J.-P.; Persello, J.; Foissy, A.; Castaing, J.-C.; Cabane, B. Effect of surface charge on the adsorption mode of sodium poly(acrylate) on alumina-coated TiO<sub>2</sub> used as coating pigment. *Colloids Surf., A* **2000**, *168*, 287–296.
- (53) Milling, A. J.; Vincent, B. Depletion forces between silica surfaces in solutions of poly(acrylic acid). *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 3179–3183.
- (54) Zaman, A. A.; Tsuchiya, R.; Moudgil, B. M. Adsorption of a Low-Molecular-Weight Polyacrylic Acid on Silica, Alumina, and Kaolin. *J. Colloid Interface Sci.* **2002**, *256*, 73–78.
- (55) Gebhardt, J. E.; Fuerstenau, D. W. Adsorption of Polyacrylic Acid at Oxide/Water Interfaces. *Colloids Surf.* **1983**, *7*, 221–231.
- (56) Meyer, E. E.; Rosenberg, K. J.; Israelachvili, J. Recent progress in understanding hydrophobic interactions. *Proc. Natl. Acad. Sci. U. S. A.* **2006**, *103*, 15739–46.
- (57) Parnas, R. S.; Chaimberg, M.; Taepaisitpongse, V.; Cohen, Y. The Adsorption of Polyvinylpyrrolidone and Polyethylene Oxide onto Chemically Modified Silica. *J. Colloid Interface Sci.* **1989**, *129*, 441–450.
- (58) Sedeva, I. G.; Fornasiero, D.; Ralston, J.; Beattie, D. A. The influence of surface hydrophobicity on polyacrylamide adsorption. *Langmuir* **2009**, *25*, 4514–21.
- (59) Farrokhpay, S.; Morris, G. E.; Fornasiero, D.; Self, P. Effects of chemical functional groups on the polymer adsorption behavior onto titania pigment particles. *J. Colloid Interface Sci.* **2004**, *274*, 33–40.
- (60) Bain, C. D.; Whitesides, G. M. Modeling Organic Surfaces with Self-Assembled Monolayers. *Adv. Mater.* **1989**, *1*, 110–116.
- (61) Siebold, A.; Walliser, A.; Nardin, M.; Oppliger, M.; Schultz, J. Capillary Rise for Thermodynamic Characterization of Solid Particle Surface. *J. Colloid Interface Sci.* **1997**, *186*, 60–70.
- (62) Joud, J. C.; Houmard, M.; Berthomé, G. Surface charges of oxides and wettability: Application to TiO<sub>2</sub>-SiO<sub>2</sub> composite films. *Appl. Surf. Sci.* **2013**, *287*, 37–45.
- (63) Takeda, S.; Fukawa, M.; Hayashi, Y.; Matsumoto, K. Surface OH group governing adsorption properties of metal oxide films. *Thin Solid Films* **1999**, *339*, 220–224.
- (64) Feng, A.; McCoy, B. J.; Munir, Z. A.; Cagliostro, D. Wettability of transition metal oxide surfaces. *Mater. Sci. Eng., A* **1998**, *242*, 50–56.
- (65) Kaggwa, G. B.; Huynh, L.; Ralston, J.; Bremmell, K. The Influence of Polymer Structure and Morphology on Talc Wettability. *Langmuir* **2006**, *22*, 3221–3227.
- (66) Chung, P. W.; Charmot, A.; Gazit, O. M.; Katz, A. Glucan adsorption on mesoporous carbon nanoparticles: effect of chain length and internal surface. *Langmuir* **2012**, *28*, 15222–32.
- (67) Chung, P. W.; et al. Importance of Internal Porosity for Glucan Adsorption in Mesoporous Carbon Materials. *Langmuir* **2015**, *31*, 7288–95.