Coating of Silica on Titania Pigment Particles Examined by Electroacoustics and Dielectric Response

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The coating of titania with a hydrous silica layer was investigated by electroacoustics, high-frequency dielectric response (DR), IR spectroscopy, and TEM microscopy. The shift in the isoelectric point measured by electroacoustics was the most sensitive indicator of silica coverage of the titania surface. Changes in the shape of the zeta potential pH dependence corresponding to formation of silica multilayers were accompanied by small changes in the IR spectra and TEM thickness. The coatings formed at 90 °C were dense and smooth and extended up to 10 nm from the titania surface. Changes in the dielectric constant of the coated pigment occurred over three domains and corresponded to changes in the nature of the adsorbing silica layer. At low concentrations, the relative permittivity of the coating layer was ∼5 but at higher concentrations it was ∼20, indicating greater hydration of the multilayer.

Introduction

Titania pigment particles are coated to control the chemical reactivity of the pigment and to protect against photocatalysis from UV radiation. Such coatings, however, change the electrokinetic properties of the coated particle and thus affect its dispersability, state of aggregation, and stability of the pigment in the dispersing medium. This paper describes the use of electroacoustics and high-frequency dielectric response to examine the electrokinetic properties of liquid-phase silica-coated titania pigments.

Coating from the liquid phase is commonly used,[1] but gas-phase coating is also employed.[2] These surface coatings usually involve oxides of silica, alumina, zirconia, or a polymer.[1] Silica coatings on titania have been the subject of many studies since Iler described the method of producing dense silica layers.[3] Furlong et al. studied the coating of rutile titania with silica by electrophoresis and found that at a concentration greater than 2.5 wt % the titania surface exhibited an isoelectric point (iep), at pH 3, similar to that of silica.[4] Reversible mobility curves were not obtained until a concentration of 5 wt % was reached. At the lower concentrations, silica adsorbed to give monolayer coverage.[4] Smooth, uniform silica coatings were relatively easy to prepare; we find a correlation between the reduction in the particle permittivity and the coating thickness as measured by TEM.

At higher concentrations, polymerization of the silicate ion enabled multilayers to be built up over the initial layer.[4] We observe the effect of multilayer formation on the pH dependence of the ζ-potential, as has been reported by other workers,[5,6] and on the dielectric permittivity of the coated particles.

Experimental Section

Materials. All glassware was cleaned by soaking in a 2% RBS solution overnight followed by rinsing with Milli-Q (Millipore) water and then soaking in a 1 M HNO_3 solution overnight, followed by several rinses with Milli-Q water.

The rutile titanium dioxide was supplied by Tiwest Joint Venture, Kwinana, WA, Australia, and is a raw titania with a very small percentage of anatase that has been doped with less than 1% $AlCl_3$ in the oxidation process. According to the manufacturers, some of the Al is within the rutile structure and some is present on the surface as a crystalline alumina coating. The raw pigment as supplied also contains coarse sand particles that are added to aid in breaking down agglomerates before surface treatment. The sand was removed by suspending the titania in Milli-Q water and shaking at its natural pH (4.1−4.3) where the pigment was well dispersed. After several minutes, the colloid was decanted off and collected. The remaining titania/sand mix was redispersed in water and the colloid was decanted and kept and the sand was discarded. The samples were then combined and decanted once more. The raw pigment was then acidified with HCl (15 M) at a volume ratio of ∼1:10 (acid /water). The suspension was boiled for 20 min and then left to flocculate. After 10 min, the supernatant was poured off and discarded. Water and HCl was then added in the same ratio and the process was repeated. Finally, water only was added and the process of heating and flocculating was repeated until the suspension no longer flocculated. The pH of the suspension was then raised to 7 with NaOH where the sample readily flocculated.

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The supernatant was poured off and the processes repeated until the conductivity was <0.1 S m^{-1}. The pigment was then evaporated in a dish at 110 °C in an oven overnight and then ground and stored in a polyethylene bottle. To determine whether the rutile surface was free of alumina, the isoelectric point of the washed pigment was determined by electroacoustics. If the iep were ≤ 6.8, then the pigment was used in coating experiments. If the iep were above pH 6.8, the pigment was rewashed by the same method.

A separate anatase titania was obtained from Bayer that contains an organic coating only. The anatase surface was washed by heating a suspension to 90 °C in NaOH (∼2−3 M), decanting, and resuspending in water. This procedure was repeated several times, and then the pH was lowered to about 5 to aid in flocculation. The sample was recovered and dried at 110 °C overnight and then measured to determine the iep. If the iep was ∼5, no further washing was performed.

Coating Process. Some samples were coated at 25 °C in the AcoustoSizer cell. The bare titania particles were dispersed in $NaNO_3$ at a conductivity of ∼0.05 S m^{-1} (∼4 mM), and a pH titration was recorded from pH 3.5 to 10. A silicate solution (0.4 M sodium metasilicate, $Na_2SiO_3{\cdot}5H_2O$) was added to give a low silica concentration ($\sim(2-5) \times 10^{-4}$ M). The pH was then readjusted to 10 with HNO_3 and left to equilibrate for 10 min. A pH titration was then conducted from pH 10 to 3, and then the pH was raised back to 10 with NaOH. At this pH, more silicate was pipetted into the suspension and the titration procedure was repeated until a limiting iep value was reached.

Samples were also coated at 90 ± 2 °C, which is known to produce smooth coatings, and then were measured at 25 °C. The bare pigment was suspended at room temperature at a volume fraction of 2% (32 g in 368 mL) in a polyethylene bottle. The pH was adjusted to 10 with NaOH and the sample was sonicated for 20 min to break up any aggregates and then was left to hydrate for a few days. The starting conductivity was usually between 0.03 and 0.07 S m^{-1}. The pH and temperature were monitored with a pH meter (CyberScan 2000) and pH probe (standard combination electrode) and a buret was used to add base or acid or coating reagent. The polyethylene bottle was placed in a beaker of boiling water and was agitated with an overhead electric stirrer. Silica was then deposited as SiO_2 in an amount between 0.1 and 10 wt % from a 1.0 M sodium metasilicate, $Na_2SiO_3{\cdot}5H_2O$, solution. The pH during addition was maintained between pH 10.0−10.5 with HNO_3. The silicate solution was added at a rate not exceeding 1.0 mmol SiO_2 per minute to avoid homogeneous precipitation. After 5−20 min stirring, the pH was then lowered to 9.2 for a period of 10−40 min for the silica coating to cure. The sample was then cooled while maintaining pH 9.2, filtered, washed, and dried at 110 °C.

Electroacoustic Measurements. The samples coated at 90 °C were dispersed in Milli-Q water at a concentration of 2 vol %. The pH was immediately adjusted to ∼8.5 (if much greater than ∼pH 9) with HNO_3. The sample was then sonicated for 10−20 min and the pH was readjusted; then, the suspension was then left to hydrate for a few days. The suspension was then poured into the AcoustoSizer-I cell and salt ($NaNO_3$) was added to give a starting conductivity of ∼0.02 S m^{-1}. Measurements were recorded at ∼pH 8.5, and then salt was added to raise the conductivity to ∼0.05 S m^{-1}. A pH titration was then recorded from pH 8.5 to pH ∼3 with HNO_3. Background corrections were not significant at these suspension concentrations and conductivities. Finally, the pH was adjusted to ∼7, and the sample was recovered by filtration and drying (110 °C).

Dielectric Response Measurements. The sample recovered from the electroacoustics measurement was dispersed in Milli-Q water at a particle volume concentration of 5%, following the same procedure as that employed to disperse the electroacoustics samples. The pH was adjusted to 7.0−8.5 or pH 3−4 and the conductivity was increased to between 0.02 and 0.07 S m^{-1} with $NaNO_3$. The sample was sonicated for a further 15 min and the pH was readjusted to the desired value. The suspension was then left to hydrate for a few days. Prior to measuring, the sample was sonicated for a further 15 min to disperse any coarse aggregates that may have formed on long standing. This was particularly necessary for samples containing higher silica concentrations. One portion of the sample was centrifuged at 10 000 rpm for ∼30 min to obtain the background solution. The background and then the sample were measured by injecting into the DR cell ensuring that all air bubbles were removed.

The conductivity measurements were made with the cell described previously.[7,8] Measurements involve injecting the sample into the cell and measuring the complex conductivity K^* of the sample as a function of frequency from 0.1 to 40 MHz with an HP 4194A impedance gain phase analyzer. Measurements were made of the complex conductivity of the colloidal suspension, $K_{sol}{}^*$, and of the background electrolyte, $K_{back}{}^* = K^\infty + i\omega\epsilon_0\epsilon_w$, as a function of frequency. Here, K^∞ is the conductivity of the background ions (which is usually frequency independent), and ϵ_w is the dielectric constant of water. For a given volume fraction, ϕ, the nondimensional dipole strength, S, per unit electric field, E, can be defined as[9]

$$S = \frac{\langle S \rangle}{4\pi a^3 \epsilon_0 \epsilon_w <E>} = \left(\frac{K_{sol}{}^*}{(K^\infty + i\omega\epsilon_0\epsilon_w)} - 1 \right) \frac{1}{3\phi} \qquad (1)$$

The dipole strength for a concentrated suspension of spheres can be calculated using the cell model formula

$$S = \frac{<S>}{4\pi\epsilon_0\epsilon_w a^3 \langle E \rangle} = -\frac{f^*}{1 + \phi f^*} \qquad (2)$$

where the dipole coefficient, f^*, is defined as

$$f^* = \frac{1 + i\omega` - \left( 2Du + i\omega` \dfrac{\epsilon_p}{\epsilon_w} \right)}{2(1 + i\omega`) + \left( 2Du + i\omega` \dfrac{\epsilon_p}{\epsilon_w} \right)}$$

Here, $Du = K_s/K^\infty a$ is the surface conductance parameter, ϵ_p is the relative particle permittivity, $\omega' = \omega\epsilon/K^\infty$ is the nondimensional frequency, and a is the particle radius. From the above formulas, it can be seen that the dipole depends on the two parameters, Du and ϵ_p. Thus, these parameters can be determined by fitting the measured dipole strength spectrum. The zeta potential, ζ, can then be calculated from the surface conductance parameter, Du, using the Bikerman equation[10]

$$Du = \frac{2}{\kappa a}\left[\cosh\left(\frac{ze\zeta}{2kT} \right) - 1 \right]\left[1 + \frac{2\epsilon(kT)^2)}{z^2\eta De^2} \right] \qquad (3)$$

where k, T, z, κ, D, and e have their usual meaning.

The coating thickness d can be calculated from the ϵ_p value using the formula

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$$\epsilon_p = \frac{\epsilon_{p(i)}}{1 + \frac{\epsilon_{p(i)}}{\epsilon_c}\frac{d}{a}} \quad (4)$$

where $\epsilon_{p(i)}$ is the permittivity of the particle core and ϵ_c is the permittivity of the coating.

Infrared Spectroscopy. The IR absorbance spectra of laboratory coated titania pigments were measured by the disk method in KBr between 400 and 4000 cm^{-1} with a resolution of 4 cm^{-1}. The sample (~0.01 g) was ground to a fine powder in KBr (~0.1 g) after drying the sample in an oven (110 °C) for about 1 h. The absorbance spectra were then measured (Bio-Rad FT Spectrophotometer, FTS-40).

Transmission Electron Microscopy. For TEM measurements, the sample (~0.05 g in 10 mL) was diluted with water at pH 8 until the suspension was no longer opaque and then was sonicated. One drop of the diluted suspension was placed on a copper grid to support the sample, the excess liquid was removed with a tissue, and the grid was left to dry. A Phillips CM12 TEM microscope was used to observe the titania coatings.

Results

TEM Observations. The coatings deposited at 90 °C were observed in TEM micrographs and were found to be dense and uniform (Figure 1). At the low silica loadings, it was difficult to obtain accurate coating thicknesses (<2 nm) because of the limited resolution of the TEM, but at higher loadings, thicknesses of up to 10 nm were observed. (See Table 2).

Electroacoustic Zeta Potential. An electroacoustic effect is generated when a MHz electric field is applied to a colloidal dispersion. For a dilute suspension of spheres, the electrokinetic sonic amplitude (ESA) is given by[11]

$$ESA = A\phi\frac{\Delta\rho}{\rho}\mu_d \quad (5)$$

where A is an instrument factor, ϕ is the particle volume fraction, $\Delta\rho$ is the density difference between the particle and solvent density (ρ), and μ_d is the particle averaged dynamic mobility. For particles with thin double layers, the dynamic mobility can be related to the zeta potential and size by

$$\mu_d = \frac{2\epsilon_0\epsilon_w\zeta}{3\eta}G(1 + f^*) \quad (6)$$

Here, G is a function that accounts for the particle inertia (see reference 11 for the detailed formula), η and ϵ ($=\epsilon_0\epsilon_w$) are the solvent viscosity and permittivity, respectively, and f^* is the function described above that represents the conductance of the double layer. In the absence of stagnant layer conduction, the f^* function is evaluated by the AcoustoSizer software using the zeta potential that gives the best fit to the dynamic mobility spectra.[11]

The pH dependence of the zeta potential for a bare titania (rutile) suspension is shown in Figure 2. The iep of this washed sample was at pH 6.7.[12] As increasing amounts of sodium silicate were added to the suspension in the AcoustoSizer cell at 25 °C, a charge reversal occurred resulting in a gradual reduction in the iep from 6.7 to a limiting value of ~2 at the highest silicate concentration. The ζ-potential became more negative and increased in magnitude up to about 7 mM silicate concentration. Above this concentration, there was a reduction in the magnitude of the zeta potential over a wide pH range. This may be due to the increase in the salt level during the titration process.

Similar effects were found for the titration of silicate onto anatase (Figure 3). The initial iep of bare anatase was ~pH 5, and a limiting iep of ~2 was also seen to occur at a concentration similar to that for rutile (Figure 2).

To eliminate the effect of increasing salt concentration from the multiple pH titrations, samples were individually

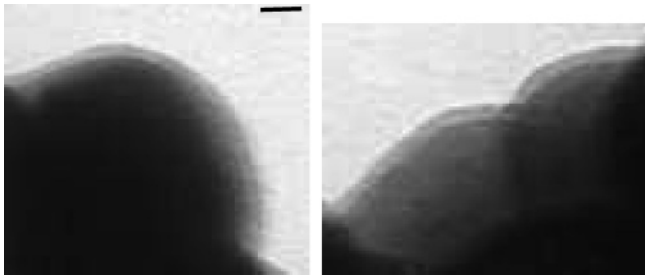

Figure 1. TEM micrograph of dense silica coatings on TiO_2 pigments. Bar represents 15 nm.

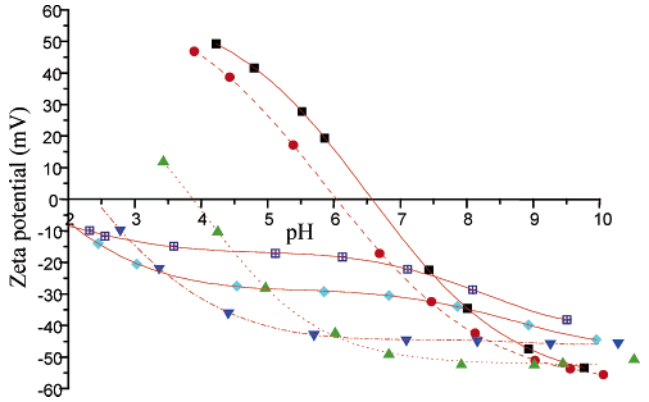

Figure 2. Variation of the particle zeta potential with pH for bare titania (rutile) as a function of added silicate concentration at 25 °C in 5×10^{-3} M $NaNO_3$. ■ 0 wt %, ● 0.016 wt %, △ 0.252 wt %, ▽ 0.643 wt %, ◇ 1.03 wt %, ⊞ 1.80 wt %.

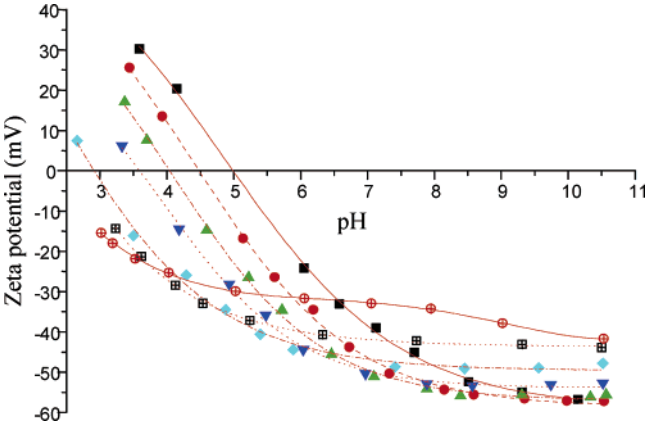

Figure 3. Variation of the particle zeta potential with pH for bare titania (anatase) as a function of added silicate concentration at 25 °C in 5×10^{-3} M $NaNO_3$. ■ 0 wt %, ● 0.043 wt %, △ 0.129 wt %, ▽ 0.259 wt %, ◇ 0.516 wt %, ⊞ 0.772 wt %, ⊕ 1.11 wt %.

(11) O'Brien, R. W.; Cannon, D. W.; Rowlands, W. N. *J. Colloid Interface Sci.* **1995**, *173*, 406.
(12) Kosmulski, M. *Adv. Colloid Interface Sci.* **2002**, *99*, 255.

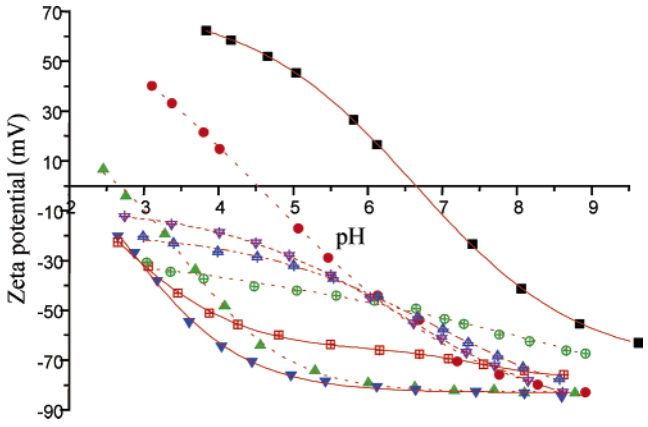

Figure 4. Variation of the particle zeta potential with pH for bare titania (rutile) and samples coated with increasing silicate concentration coated at 90 °C in 5 × 10^{-3} M $NaNO_3$. ■ 0 wt %, ● 0.19 wt %, △ 0.66 wt %, ▽ 0.94 wt %, ⊞ 1.7 wt %, ⊕ 2.47 wt %, + in a △ 3.45 wt %, + in a ▽ 7.00 wt %.

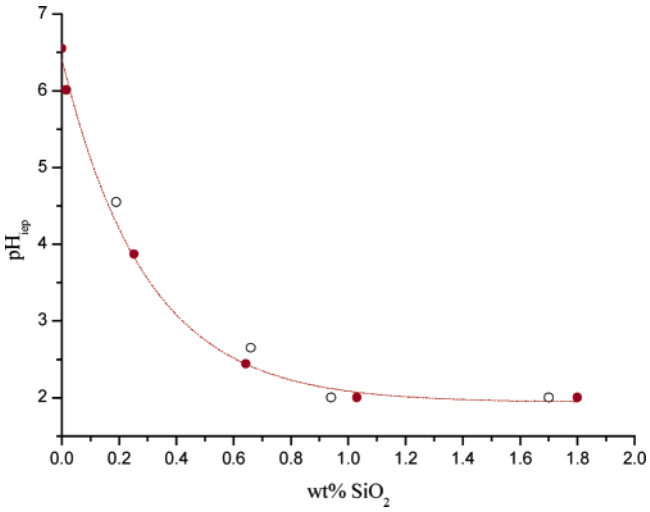

Figure 5. Change in the isoelectric point of rutile as a function of added silicate concentration coated at 25 °C (●) or at 90 °C (○).

coated with increasing concentrations of silicate at 90 °C and then were measured at 25 °C at similar conductivities of ~0.06 S m^{-1} (5 mM $NaNO_3$). Again, the isoelectric point shifted from pH 6.8 for the uncoated rutile to pH 2 with 1 wt % SiO_2 (Figure 4). Comparison between the two sets of data (Figure 5) indicates that 1 wt % is sufficient to create a silica surface.

At more than 1 wt % silica, the zeta potentials between pH 8 and 3 again decrease in absolute value. In this case, the effect cannot be due to the electrolyte concentration, which was held constant. We ascribe it to a change in the nature of the silica surface with multilayer formation, as revealed further by dielectric response measurements.

Dielectric Response. The high-frequency dielectric response of a suspension of uncoated rutile is shown in Figure 6 at two different $NaNO_3$ electrolyte concentrations. The high-frequency limit gives a constant ϵ_p value of 118, consistent with a bare rutile surface.[13] The shape of the curves is very sensitive to the electrolyte concentration, reflected in different *Du* values. At the low salt concentration, more

(13) *CRC Handbook of Chemistry and Physics*; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 2003.

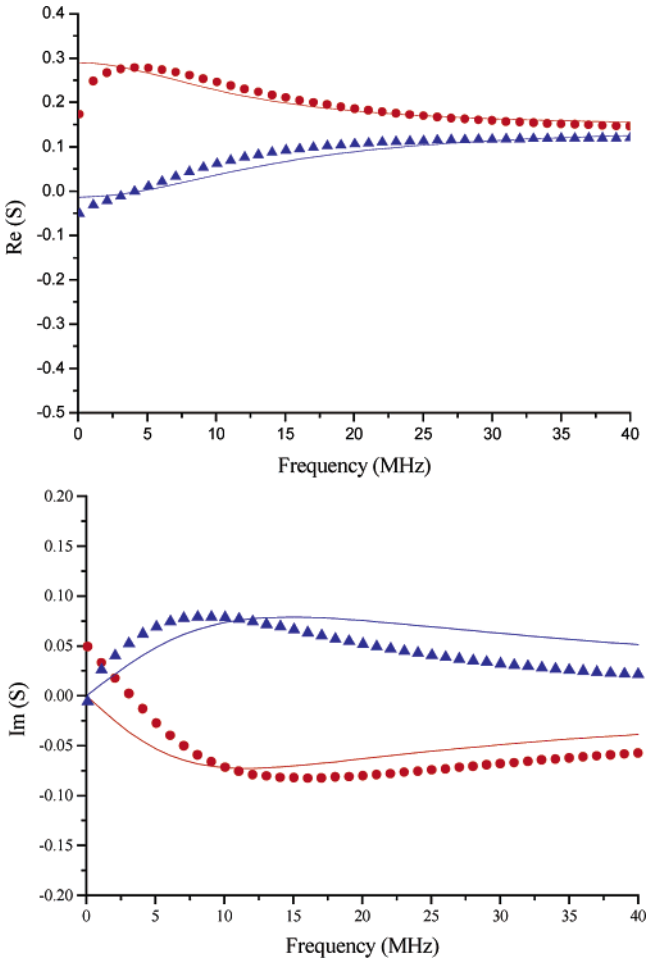

Figure 6. Dielectric response showing real (top) and imaginary (bottom) parts of the dipole strength of bare titania at pH 3.4 in $NaNO_3$. K^{∞}, *Du*, ϵ_p: ● 0.0426, 1.1, 118; ▲ 0.0758, 0.48, 118.

of the field is conducted by ions in the double layer, that is, by surface conduction. As the bulk electrolyte concentration increases, the ratio of surface conduction to bulk conduction, *Du*, decreases.

The effect of silica coating on the dielectric permittivity of the particles is seen clearly in the dielectric response curves for suspensions of the particles coated at 90 °C (Figure 7). As the silica concentration increases, the high-frequency limit of the real component (top of Figure 7) decreases, indicating a decrease in the particle permittivity. The low-frequency limit also decreases, indicating a reduction in the *Du* value, and would reach a limit of −0.5 as *Du* approaches zero. The measurements were made on the individually coated samples that were then suspended in 4−5 mM $NaNO_3$ electrolyte, so the conductivities are all about the same and the relaxation effect seen in the imaginary component occurs at the same frequency. The change in *Du* hence reflects a change in the surface properties of the particles. Examination of the numerical data (Table 1) reveals that dielectric response measurements are less sensitive than the electroacoustic effects to changes in the surface coating. Each of the samples coated with <1 wt % silica give dielectric response curves fitted to permittivity values of 107−108, even though these samples are only partially coated with silica as indicated by the electroacoustic iep results (recall Figure 5). However, above 2 wt % the permittivity decreases

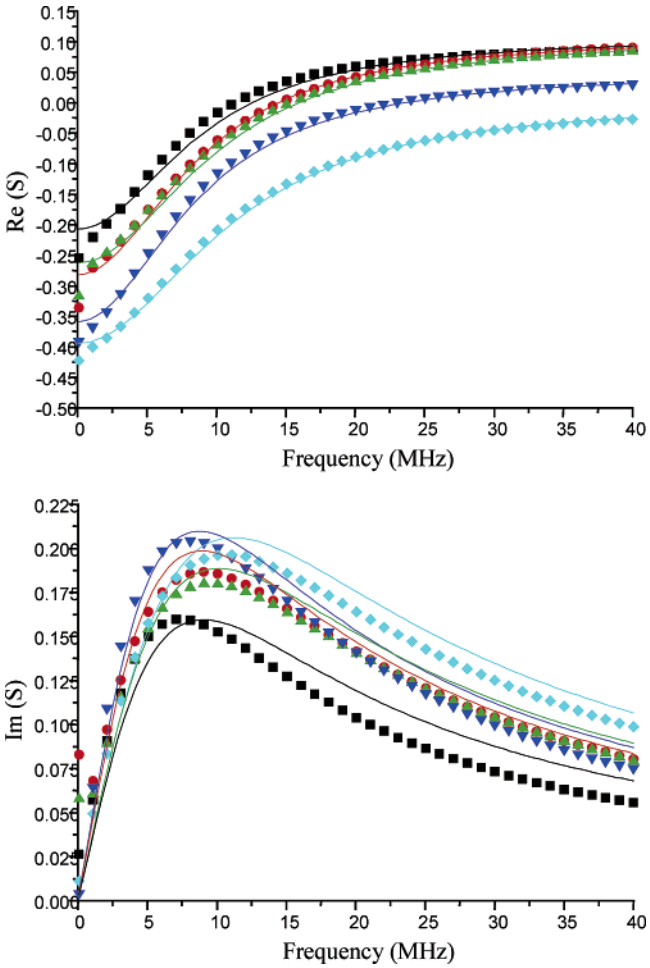

Figure 7. Particle dipole showing real (top) and imaginary (bottom) components as a function of frequency for bare rutile coated with silicate at 90 °C measured in 4−5 mM $NaNO_3$ between pH 7−8: ϵ_p, *Du*. ■ 107, 0.24; ● 107, 0.17; ▲ 107, 0.19; ▼ 91, 0.10; ♦ 80, 0.07.

Table 1. Values of Particle Permittivity, Surface Conductance Parameter, Surface Potential, and Zeta Potential for 260-nm Rutile Titania Particles Coated at 90 °C with Various Amounts of Silica

wt % SiO_2	iep	pH	K^∞ (S m^{-1})	$\epsilon_p \pm 2$	$Du_{DR} \pm$ 0.005	$\lvert\psi_{DR}\rvert$ (mV)	$\lvert\zeta\rvert$ (mV)
0.19	4.55	8.12	0.05345	107	0.241	95	80
0.66	2.65	7.79	0.05605	107	0.167	85	83
0.94	2.0	7.24	0.04835	107	0.28	99	90
1.70	2.0	7.56	0.06295	107	0.185	88	75
2.47	2.0	7.93	0.05649	98	0.202	89	62
3.45	∼2.0	7.69	0.05495	91	0.0991	66	73
		4.91	0.06924	91	0.005	17	30
7.00	∼2.0	7.88	0.06918	80	0.070	60	65

with increasing silica deposition.

A possible explanation for the apparently low zeta potentials with increased silica on the surface would be the presence of stagnant layer conduction. If ions conduct within the stagnant layer inside of the shear plane from which the electrokinetic zeta potential is measured, then the effective electric field applied in the electroacoustic technique is attenuated and the calculated zeta potential is lowered. To test this hypothesis, measurements were made on two samples coated at 90 °C, with 0.66 and 2.47 wt % Si, respectively, at the low electrolyte concentration of 1.9 mM $NaNO_3$ (K^∞ = 0.023 S m^{-1}) where the effect should be greater. In both cases, the zeta potential from electroacoustics and the surface potential evaluated from the *Du* value

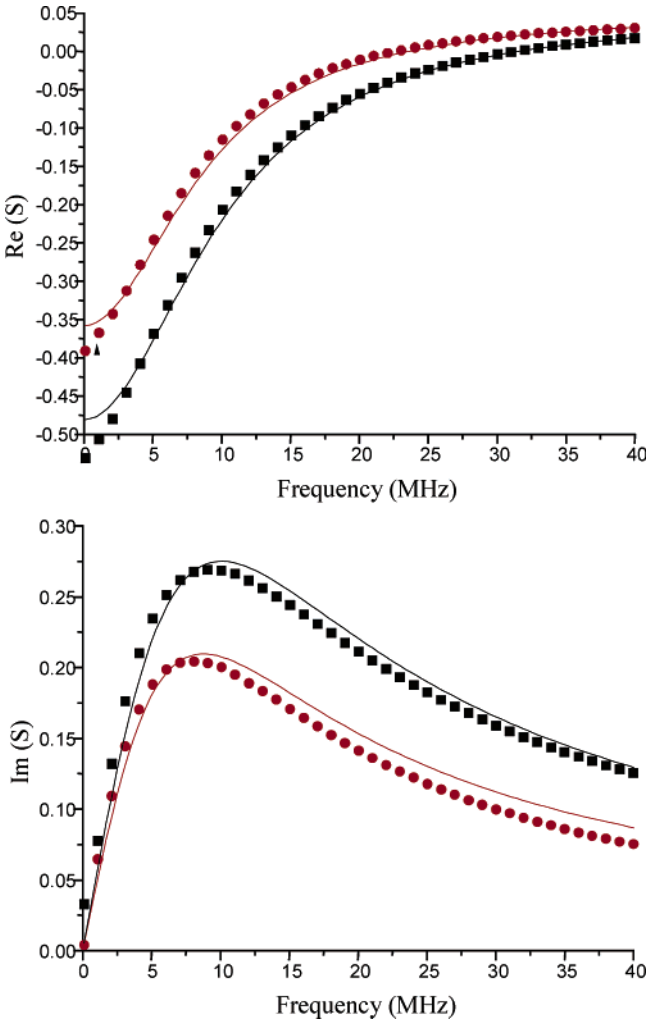

Figure 8. Particle dipole showing real (top) and imaginary (bottom) components as a function of frequency and pH for bare rutile coated with silicate at 90 °C measured in 4−5 mM $NaNO_3$. pH, ϵ_p, K^∞, *Du*. ● 4.9, 91, 0.0692, 0.005; ■ 7.69, 91, 0.0549, 0.099.

obtained from the dielectric response were in reasonable agreement (−110 and −121 mV for the first sample and −100 and −116 mV for the second) to indicate that stagnant layer conduction was not significant. Hence, the reduction in the zeta potential to −(60−70) mV must reflect a change in the surface properties of the adsorbed silica after the surface is saturated with a monolayer, reflected by an iep at pH 2.

In another test of the self-consistency of the data, the 90 °C coated sample with 3.45 wt % silica was measured by dielectric response at two different pHs (Figure 8). Both measurements gave the same value of the permittivity (ϵ_p = 91) but at pH 4.9 a much smaller value of *Du*, and hence of the surface charge, than at pH 7.7, consistent with the much smaller zeta potential observed in the electroacoustic titration of this sample (Figure 4).

Coating Thickness. The fitted permittivity value, ϵ_p, from dielectric response enables an estimate of the thickness of the coating to be calculated. Taking thicknesses *d* from the TEM observations, the value of ϵ_c of the silica layer was varied in the analysis of the dielectric response to obtain the same thickness. In Table 2, the coating thickness, *d*, from the relative permittivity of the coated particle, ϵ_p, for a range

Table 2. Values for the Coating Thickness, *d*, Calculated from the Measured Permittivity, ϵ_p, for a Range of ϵ_c Values, along with the Coating Thickness Observed from TEM, d_{TEM}

SiO_2 (wt %)	d_{TEM} (nm)	*d* (nm) $\epsilon_c = 4.5$	*d* (nm) $\epsilon_c = 10$	*d* (nm) $\epsilon_c = 20$	*d* (nm) $\epsilon_c = 25$
0	0	0	0	0	0
0.19	<1	0.50	1.1	2.2	2.8
0.66	~1	0.50	1.1	2.2	2.8
0.94	2.1	0.505	1.1	2.2	2.8
1.70	3.2	0.50	1.1	2.2	2.8
2.47	4.0	1.0	2.2	4.2	5.6
3.45	6.5	1.5	3.3	6.6	8.28
7.0	10.5	2.4	5.2	10.4	13.1

of ϵ_c values is compared to the thickness obtained from TEM, d_{TEM}. If values of 4.5 or 10 for ϵ_c for amorphous silica were used, the calculated thickness was less than that observed in the TEM. The value of ϵ_c required to match the TEM thickness was $\epsilon_c = 20 \pm 2$ for samples coated at 90 °C with a thickness of >2 nm.

Infrared Spectra. As the coating thickness increases, the IR spectra (Figure 9) between 1000 and 1300 cm^{-1} display two peaks that increase in intensity, assigned to Si−O−Si and $Si-O^-$ vibrations.[14]

Discussion

The pH dependence of the zeta potential and the consequent determination of the isoelectric point provide a reliable and sensitive indication of the surface coating of silica on the titania particles. As up to 1 wt % silica is added to the titania suspensions, the zeta potential becomes progressively more negative and the iep shifts to lower pH (Figures 2 and 3). Regardless of whether the coating is performed at 25 or at 90 °C, 1 wt % of SiO_2 is sufficient to completely coat the particles so that a silica surface appears with an iep at pH 2 (Figure 5). If the titania particles are assumed to be spherical, and the silica surface has the density of quartz, this corresponds to a coating layer thickness of 0.7 nm. If the particles are nonspherical, they would have an increased surface area, and hence the layer would be thinner, while if the silica layer is less dense than quartz, the calculated thickness would be larger.

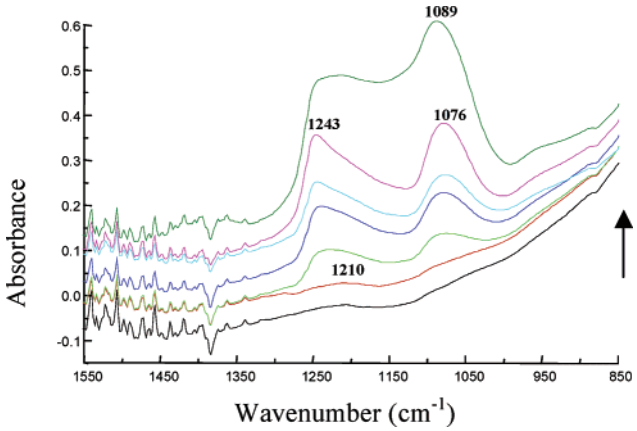

Figure 9. IR spectra of silica coated TiO_2 pigments.

With these thin layers, the dielectric response spectra are less sensitive than the zeta potential to the extent of the silica coating (Figure 7 and Table 1). Whether the coverage is incomplete (<1 wt %) or greater than a monolayer (1.7 wt %), the dielectric response can be fitted with a constant particle permittivity of 107−108, reduced from that of 118 for rutile itself. This reduction in the particle permittivity corresponds to a permittivity of 6 for a 0.7-nm silica layer (eq 6). The surface conductance parameter Du_{DR} is similarly not very sensitive to the extent of the silica coverage.

The shift in the iep with silica coating on titania is well-known.[4−6,15] What the present results reveal is the change in the nature of the adsorbed silica surface as multilayers are deposited. The very negative zeta potential is reduced in magnitude. This can be attributed to some polymerization of the silica to form uncharged siloxane groups (Si−O−Si) in place of ionizable silanol groups (Si−OH). At the same time, this multilayer becomes more hydrated, as reflected in the increased effective dielectric permittivity calculated for the silica layer.

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