SCAA 44th Annual Conference Call for Papers

The Surface Coatings Association of Australia will hold its 44th Annual Conference in Canberra, Australia.

The conference will be held August 6-9, 2003 at the Canberra Convention Centre. The theme of the conference will be "Capital Ideas for Coatings". All interested companies and individuals are invited to submit papers for consideration. Papers should follow the conference theme. Other topics, for example, the use of computers in the paint industry, industry-specific sales, marketing and manufacturing techniques, color measurement or matching technology, etc., are also welcome. Anyone interested in presenting a paper should contact the Technical Coordinator and submit a summary by January 31, 2003. These papers selected for presentation must be received by April 30, 2003. For more contact Lynsey Bailey, Mirtomite Pty Ltd; +61 2 97 95.7751; email: lbailey@mirtomite.com.au.

Cal Poly to Offer Coatings Winter Short Course

The Polymers and Coatings program at Cal Poly Pomona is offering a winter short course, San Luis Obispo, to offer "A Coatings Science and Technology" short course February 3-7, 2003.

The one-week course will cover many aspects of coating technology including resins chemistry, pigments and fillers, additives, application aspects, and as well as have some coating with emphasis on liquid coatings.

The short course will bring together a mix of academic and industrial persons in the field to guarantee both fundamental and application aspects are addressed with equal emphasis. Other coating technologies (e.g., powder coating, a workshop on formulated adhesion technologies) will be included. Course Logistics: Contact Lynsey Bailey, Mirtomite Pty. Ltd.; +61 2 97 95.7751; email: lbailey@mirtomite.com.au.

ASTM D01 Minisymposium Presented January 14, 2003

ASTM Committee D01 on Paint and Related Coatings, Materials, and Applications will host its annual 90-minute minisymposium on January 14, 2003 at the Embassy Suites Hotel, Ft. Lauderdale, FL. Entitled "New Concepts for Reducing VOCs," the minisymposium will feature talks by Rocky Prior and James C. Berry.

Rocky Prior, Vice President and General Manager of Southern Diversified Products, Hauppauge, NY, will speak on "Advanced Polymer Technology for VOC-Free Waterborne Paints and Coatings." Low VOC interior wall paints based on new latexes made from natural products will be discussed.

James C. Berry, Manager of the U.S. EPA, will discuss "Micelles. A New Tool to Remove VOCs." Active in D01, Mr. Berry's EPA group originated many of the rules and regulations for VOCs in paints. Since retiring in 1996, he has authored several papers on various aspects of abatement of emissions from paints and related products. New technology based on biocatalytic oxidation will be presented.

UMR Coatings Institute Announces 2003 Short Course Schedule

The Coatings Institute at the University of Missouri-Rolla, Rolla, MO, has announced its Coatings Short Course schedule for 2003.

The course schedule is as follows:

"The Basic Composition of Coatings" March 31-April 4 and September 8-12

This course is designed to introduce the newcomer, as well as those involved in raw material manufactures, sales, and technical service, to the technical aspects of paint manufacturing, testing, and use. Topics of discussion will include the history of paint materials used in manufacture, simple formulating techniques that can be put to immediate use, introduction to the equipment used to make and test modern aqueous coatings, modern chemical instrumentisation as applied to coatings, simple accounting that allows beginners to start on a stable economic basis. A course fee of $995 includes classroom materials and instruction, coffee breaks, and refreshments.

"Introduction to Paint Formulation" May 12-16 and September 29-October 3

This five-day course is described as an intensive walk through the basic steps of paint formulation, from understanding the properties of an actual laboratory formulation. Attendees will have the opportunity to study and experiment with basic raw materials and their influence on the performance of the finished coating, formulating, and testing of coatings in the laboratory to master the special demands of the job. Limitations of plant production equipment and formulation variables for moving a coating from the lab to the plant, and modern chemical instrumentisation as applied to coatings.

A course fee of $995 includes classroom materials and instruction, coffee breaks, and refreshments.

For additional information or a registration form contact, 573.341.4419, email: mvanishing@umr.edu, or visit http://webcoatings.org/ -coatings.

Unifying Model for Associative Thickeners Influences on Waterborne Coatings: I. Competitive Adsorption of Nonionic Surfactants and HEUR Thickeners on Titanium Dioxide Pretreated with Inorganic Stabilizers and Organic Oligomeric Dispersants

Ming-Ren Tang, Mao Chen, and J. Edward Glass—North Dakota State University
John G. Dickinson—E. I. DuPont de Nemours & Co. Inc.

INTRODUCTION

In most practical cases, dispersions are complex systems containing more than one type of dispersed particle, and a combination of different surfactants and polymers are used to stabilize the particles. Competitive adsorptions occur in this complex fluid, with the more surface-active components displacing less surface-active ones previously adsorbed for kinetic reasons. The competitive adsorption of polymer chains, and their displacement at liquid-solid interfaces, has been reviewed with respect to both theoretical and experimental consideration. It has been observed in the competitive adsorptions of sodium dodecylsulphate (SDS) and ethoxylated nonylphenol (NP-EO) blends on TiO2; that NP-EO:H alone is not adsorbed significantly on TiO2; however, the amount of NP-EO:H adsorbed increased by more than 50 times in the presence of lower amounts of SDS, but decreases at higher SDS concentrations. Adsorption on TiO2 is reported to be affected by the order of addition. The competitive adsorption of poly(acrylic acid) and ethyl(hydroxyethyl)cellulose blends.

The dispersion of pigments is an important factor in the performance of a coating. Titanium dioxide, the hindering pigment in a coating, is easily flocculated in aqueous solutions below its isoelectric point (IEP). Above the IEP, it may be flocculated by low salinity gradients. To stabilize such a high energy dispense phase, it is treated with surfactant and an oligomeric polyacrylic dispersant. The adsorption of surfactant and dispersant increases the stability of the dispersion by increasing the electrostatic repulsion between particles, but in the presence of a nonadsorbing thickener, the stability of the TiO2 is often not enough stable to ensure good applied film gloss.

In Part I of this series, the interactions among model hydrophobically modified ethoxylated urethane (HEUR) thickener, waterborne TiO2 surfaces, and 123 nanometer latex particles were studied. In those experiments, three different surfactants (the type of use in waterborne latex coatings) were added, separately, with model HEURs to the latex dispersion.

Presented at the SPI Annual Meeting of the Federation of Societies for Coatings Technology, on October 23-25, 1999 in October, F.

AdSORption on the latex's surface was determined primarily by both the relative hydrophobe sizes of the HEUR thickener and the nonionic surfactant, and by their relative concentrations. The objectives of this study include quantifying the influence of the metal oxide (Al2O3, ZrO2, and TiO2) treatment of TiO2 on the adsorption of the oligomeric polyacrylic dispersant when the chemical compositions of the alpha-olefin/maleic acid co-oligomers are changed. These changes are then quantified for their influence on the amounts of
different components (pigment, dispersant, surfactant, and associative thickener) are present in the disperse phase systems. Step-growth (S-G) HEURs, that also will be studied, have a broad molecular weight distribution that encompasses unreacted poly(oxyethylene) (POE) starting materials. The surfactant is very low in molecular weight; and the one used in this study, CH2=CH(CH2)9-C-(CH2)9-C(OH)-(CH2)9-OH (referred to as CH2=C(CH2)8=OHEO3H) in the rest of this article, has a molecular weight average of 646.96. This average encompasses 11 different components. Thus, both surfactants and thickeners contained a multitude of molecular weight components.

In a prior study, commercial HEURs were observed to individually adsorb on dispersant pretreated titanium dioxide; however, the structures of the commercial HEURs were unknown, and competitive adsorptions in mixtures containing nonionic surfactants were not investigated. Through the use of a novel, organic solvent-based, size exclusion chromatographic (SEC) technique, separation and quantification of the associative surfactant and thickening can be realized.

**EXPERIMENTAL**

**Starting Materials**

Maleic anhydride (Figure 1) alternating with different hydrocarbon groups are examined as low molecular weight co-oligomer dispersants. Their molecular weights are listed in Table 1. The co-oligomers were synthesized using the styrene/maleic acid co-oligomer (with the strong UV chromophore of the phenyl unit) examined in this study to provide a double check on adsorption data obtained from the weaker carbonyl absorption band. The co-oligomerized maleic anhydrides were hydrolyzed to maleic acid following a previously described procedure.\(^1\) The surfactant, CH2=C(CH2)9=OHEO3H (an ethoxylated octylphenol with an average of 9-10 oxyethylene units) was obtained from Union Carbide. The synthesis, characterization, and isolation of the model un-HEURs and step-growth HEURs (Scheme 1) have been described;\(^2\) their compositions and characteristics are listed in Table 2. An excess of diisocyanate is used in the synthesis of the narrow molecular weight and requires numerous extractions to remove this excess and its reaction products. A ratio of four equivalents of diisocyanates to three disil units of ca. 200 repeating units produces S-G HEURs with broad molecular weight distribution products. Given the many mechanisms for degradation of HEUR thickeners, their molecular weight reproducibility within a series is good.

**Procedures**

Aqueous stock solutions of associative thickener were prepared by properly dispersing the "fine" powder particles in DI water and rolling the solutions for 48 h. Pigment dispersions were prepared at 70% solids, according to the following formula which was representative of each pigment preparation: 700 g titanium dioxide, 10.5 g dispersant (20 wt% aqueous solution), and 290 g distilled, deionized water.

The dispersant solution and about 30 ml of DDI water were added to a metal grinding vessel. The pigment and DDI water were added slowly with mixing. After the addition of all components, the slurry was dispersed at high speed for about five minutes, and the fineness of the grind was obtained as NS units (>7 N is acceptable in the ASTM 1210 test procedure).

**Adsorption Studies**

Dispersant adsorptions were studied at 0.3 g/100 g TiO2 concentration. The UV absorbance at 204 nm of the maleic acid group was chosen as the concentration indicator (Figure 2a). The UV band of the carbonyl is broad; therefore, the amounts of dispersant adsorbed were the least sensitive data generated in this study. The SEC technique cannot be easily used to study the adsorption of dispersant. The dispersant contains carbonyl anions and is not soluble in organic solvents. The dispersants also were likely to adsorb irreversibly\(^3\) on the SEC column.

The SEC technique was used to measure the adsorption of the nonionic surfactant, CH2=C(CH2)9=OCH3, on titanium dioxide stabilized by hydrophobic dispersants. Surfactant adsorption also was measured by UV spectrophotometry. The SEC technique monitored the peak area at 2.75 minutes elution time for CH2=C(CH2)9=OCH3 in the UV technique, the absorbance peak height at 278 nm (aromatic group of surfactant) was chosen to monitor the concentration (Figure 2b).

**Competitive Adsorptions**

The chromatography system consisted of a Waters 510 HPLC pump, a Waters U6 K injector with a 2 ml loading loop, a Waters 481 differential refractometer, a Waters 730 data module, a one-phase of HPLC grade tetrahydrofuran, a flow rate of 1.0 ml/min, a column temperature of 30°C, an injection volume of 200 ml, and a Shodex KF-8080 (column: 800 x 7.8 mm) size exclusion column. The refractive index difference between the reference and sample cell was used to analyze the adsorption and all analyses were performed in the high performance liquid chromatography (HPLC) mode to obtain peak areas. Calibration curves were prepared using aqueous surfactant and thickener solutions between 0.1 and 1.0 wt%.

Adsorption data at 25°C were determined from diluted original pigment dispersions, originally at a constant pigment content of 0.1 volume fraction, with a constant surfactant concentration of 0.8 wt% and varying HEUR thickener concentrations. Equilibration in the competitive adsorption studies were reached by rolling dispersions with all components for 24 hr. The pigment dispersions were centrifuged with a DuPont Servall (RC-5B) refrigerated super centrifuge at 7°C to 10°C and 10,000 rpm for 30 min. Approximately one gram of the supernatant was weighed into a 20 ml scintillation vial. The supernatant was diluted with tetrahydrofuran (THF) to the concentration range of the calibration curves, and the solution was analyzed with the SEC method (Figure 2c). The SEC data were obtained after dilution of one gram of supernatant with nine grams of THF; the UV data were obtained after five grams of supernatant were diluted with five grams of methanol. All adsorption studies were done in triplicate; the data variance was ±3%.

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**Table 1** — Molecular Weights of Maleic Acid (C9H6O4) Dispersants by Size Exclusion Chromatography

<table>
<thead>
<tr>
<th>Dispersant</th>
<th>Mn</th>
<th>Mw</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>C9H6O4MAcid</td>
<td>1500</td>
<td>2500</td>
<td>1.7</td>
</tr>
<tr>
<td>C9H6O4MAcid</td>
<td>2400</td>
<td>3200</td>
<td>2.4</td>
</tr>
<tr>
<td>Styrene/Maleic Acid</td>
<td>4400</td>
<td>9300</td>
<td>2.1</td>
</tr>
</tbody>
</table>

**Scheme 1** — Synthesis of model narrow molecular weight distribution hydrophobe-modified ethyleneurethane (unilink) thickeners.

**Table 2** — Molecular Weights of NH-CONH-CH2=CH2-CH2=CH-NH-CONH-CH2=CH2-CH2=CH-NH-CONH-CH2=CH2-CH2=CH-NH-CONH-NH-HEUR Associative thickeners by Size Exclusion Chromatography

<table>
<thead>
<tr>
<th>R-Su</th>
<th>Su</th>
<th>C9H6O4 MAcid</th>
<th>Mn</th>
<th>Mw</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>R-</td>
<td>C9H6O4 MAcid</td>
<td>5400</td>
<td>3460</td>
<td>1.4</td>
<td></td>
</tr>
<tr>
<td>R-</td>
<td>C9H6O4 MAcid</td>
<td>2700</td>
<td>3460</td>
<td>1.4</td>
<td></td>
</tr>
<tr>
<td>R-</td>
<td>C9H6O4 MAcid</td>
<td>2400</td>
<td>3740</td>
<td>1.1</td>
<td></td>
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<tr>
<td>R-</td>
<td>C9H6O4 MAcid</td>
<td>3500</td>
<td>3740</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td>R-</td>
<td>C9H6O4 MAcid</td>
<td>3200</td>
<td>3570</td>
<td>1.1</td>
<td></td>
</tr>
</tbody>
</table>

**Figure 1** — General structures of styrene/maleic acid copolymer and α-olefins/maleic acid model dispersants. n = 3 or 7, referred to as D4 and D8.
M.R. Tang et al.

model HEUR associative thickeners and nonionic surfactant adsorbed under competitive conditions on the pretreated BS-5 HEUR. The competitive adsorption between associative thickener and surfactant is complicated by their similarities in structures, and by the fact that four different components (pigment, dispersant, surfactant, and associative thickener) are present in the disperse phase systems. Steep-growth (S-G) HEURs, that also will be studied, have a broad molecular weight distribution that encompasses unreacted poly(oxyethylene) (POE) starting material.\(^1\) The surfactant is very low in molecular weight; and the one used in this study, CH\(_2\)(CH\(_2\))\(_2\)-CH(CH\(_2\))\(_2\)-O-CH\(_2\)(CH\(_2\))\(_4\)OH (referred to as CH\(_2\)(CH\(_2\))\(_4\)H), was used in the rest of this paper, has a molecular weight average of 466.96. This average encompasses 11 different components.\(^2\) Thus, both surfactants and thickeners contain a multitude of molecular weight components.

In a prior study,\(^2\) commercial HEURs were observed to individually adsorb on disperse pretreated titanium dioxide; however, the structures of the commercial HEURs were unknown, and competitive adsorptions in mixtures containing nonionic surfactants were not investigated. Through the use of a novel, organic solvent-based, size exclusion chromatographic (SEC) technique, separation and quantification of the associative thickener and surfactant can be realized.

**Experimental**

Maleic anhydride (Figure 1) alternating with different hydrocarbon groups are examined as low molecular weight co-oligomer dispersants. Their molecular weights are listed in Table 1. The molar ratios were chosen to conform to the styrene/maleic acid co-oligomer (with the strong UV chromophore of the phenyl unit) is examined in this study to provide a double check on adsorption data obtained from the weaker carboxylate absorption band. The co-oligomerized maleic anhydrides were hydrolyzed to maleic acid following a previously described procedure.\(^1\) The surfactant, CH\(_2\)(CH\(_2\))\(_4\)OH (an ethoxylated octylphenol with an average of 9-10 oxyethylene units) was obtained from Union Carbide. The synthesis, characterization, and isolation of the monofunctional HEURs and steep-growth HEURs (Scheme 1) have been described;\(^2\) their compositions and characteristics are listed in Table 2. An excess of diisocyanate is used in the synthesis of the narrow molecular weight and requires numerous extractions to remove this excess and its reaction products. A ratio of four equivalents of diisocyanates to three diol units of ca. 200 repeating units produces S-G HEURs with a broad molecular weight distribution. For this reason, the mechanisms for the depression of HEUR thickeners, their molecular weight reproducibility within a series is good.

**Procedure**

Aqueous stock solutions of associative thickener were prepared by properly dispersing the "fine" powder particles in DI water and rolling the solutions for 463 h. The pigment dispersions were prepared at 70% solids, according to the following formulation which was representative of each pigment dispersion: 700 g titanium dioxide, 10.5 g dispersant (20 wt% aqueous solution), and 290 g distilled, deionized water.

The dispersant solution and about 30 ml of DDI water were added to a metal grinding vessel. The pigment and water were added slowly with mixing. After the addition of all components, the slurry was dispersed at high speed for about five minutes, and the fineness of the grind was obtained as NS units (>7 N is acceptable in the ASTM 1210 test procedure).

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Dispersant adsorptions were studied at 0.3 g/100 g TiO\(_2\) concentration. The UV absorbance at 204 nm of the maleic acid group was chosen as the concentration indicator (Figure 2a). The UV band of the carboxyl is broad; therefore, the amounts of dispersant adsorbed were the least sensitive data generated in this study. The SEC technique cannot be easily used to study the adsorption of dispersant. The dispersant contains carboxylate anions and is not solvable in organic solvents. The dispersants also were likely to adsorb irreversibly\(^2\) on the SEC column.

The SEC technique was used to measure the adsorption of the nonionic surfactant, CH\(_2\)(CH\(_2\))\(_4\)OH, on titanium dioxide stabilized by hydrophobic dispersants. Surfactant adsorption also was measured by UV spectrophotometry. The SEC technique monitored the peak area at 7.25 minutes elution time for CH\(_2\)(CH\(_2\))\(_4\)OH/HEUR in the UV technique, the absorbance peak height at 278 nm (aromatic group of surfactant) was chosen to monitor the concentration (Figure 2b).

**Competitive Adsorptions**

The chromatography system consisted of a Waters 510 HPLC pump, a Waters U/6 injector with a 2 ml loading loop, a Waters 4801 differential refractometer, a Waters 730 data module, a one-phase of HPLC grade tetrhydrofuran, a flow rate of 1.0 ml/min, a column temperature of 30°C, an injection volume of 200 ml, and a ShodexKF-801 (elution volume: 200 ml) size exclusion column. The refractive index difference between the reference and sample cell was used to analyze the adsorption and all analyses were performed in the high performance liquid chromatography (HPLC) mode to obtain peak areas. Calibration curves were prepared using aqueous surfactant and thickener solutions between 0.1 and 1.0 wt%.

Adsorption data at 25°C were determined from diluted original pigment dispersions, originally at a constant pigment content of 0.1 volume fraction, with a constant surfactant concentration of 0.5 wt% and varying HEUR thickener concentrations. Equilibria in the competitive adsorption studies were reached by rolling dispersions with all components for 24 h. The pigment dispersions were centrifuged at 20,000 rpm for 30 min. Approximately one gram of the supernatant was weighed into a 20 ml scintillation vial. The supernatant was diluted with tetrahydrofuran (THF) to the concentration range of the calibration curves, and the solution was analyzed with the SEC method (Figure 2c). The SEC data were obtained after dilution of one gram of supernatant with nine grams of THF; the UV data were obtained after five grams of supernatant were diluted with five grams of methanol. All adsorption studies were done in triplicate; the data variance was ±3%.

![Figure 1 - General structures of styrene/maleic acid co-oligomer and α-maleic/maleic acid model dispersants.](image)

![Figure 2a - Calibration curve of dispersants by UV absorbance at 204 nm with different dispersant concentration. Symbol: (●) CH\(_2\)(CH\(_2\))\(_4\)OH, (○) CH\(_2\)(CH\(_2\))\(_4\)H, (□) CH\(_2\)(CH\(_2\))\(_4\)H/MACd.](image)

![Figure 2b - Calibration curve of CH\(_2\)(CH\(_2\))\(_4\)OH/HEUR concentration at 278 nm with different concentration diluted with 50/50 weight ratio mixture of water/methanol solution.](image)

![Figure 2c - Calibration curve of CH\(_2\)(CH\(_2\))\(_4\)OH/HEUR concentration at 278 nm with different concentration diluted with 50/50 weight ratio mixture of water/methanol solution.](image)
RESULTS AND DISCUSSION

Structural Influence of the Organic Oligomeric Acid and Metal Oxide Treatment on Adsorption

Titanium dioxide reacts with organic materials by electron transfer to form amorphous phases. From this type of degradation, it is a common practice for the manufacturer to pretreat TiO₂ with either Al₂O₃ or SiO₂ or both. These parameters are examined using model pHUR thickener. It also is a common practice to add an organic dispersant (e.g., an acrylic or methacrylic acid oligomer or an α-olefin/maleic acid copolymer). The adsorption of the metal oxide-treated TiO₂ grind with a greater number of unneutralized acids to hydrogen bond or acid-base interact with the pigment surface. The maleic acid co-oligomer adsorbs significantly more than the oligomeric methacrylic acid dispersant. The co-oligomer also possesses hydrophilic units to interact with the conventional surfactant and associative thickeners on the TiO₂ surface.

Aluminum oxide treatment of the TiO₂ surface is the most common commercial type, so the adsorption behavior of maleic acid co-oligomers on Al₂O₃-treated TiO₂ will be examined first. Three types of maleic acid dispersants were used. The [CH₃(CH₂)₄]₄ maleic acid (hereafter referred to as D8/MA) dispersant adsorbs more than the smaller α-olefin [(CH₂)₇(CH₄)₄] maleic acid (D4/MA) while the adsorption of the styrene-co-oligomer (Table 1) is very low from 9.3 pH dispersions (figure 3). The dispersants vary in the size of the pendant hydrocarbon group and the number of double bonds in the main chain. These groups in the early decades of surface chemistry have been approximated as 2.5 carbons based on its surface activity. Using this criterion, the adsorption behavior of the dispersants on Al₂O₃-treated TiO₂ is determined by the hydrophobe size of the dispersant. This would consist of Al₂O₃-7 for ZrO₂ and Al₂O₃-8 for the other oligomer treated with the smaller α-olefinic acid. This is consistent with a medium of lower dielectric constant to the contiguous acid. This complemented by the repulsion of two contiguous anionic groups in maleic acid salts, facilitates maintenance of half of the carboxylate groups as unionized acids, even at a dispersion pH of 9.3.

Molecular weight also is an important parameter in the adsorption process. The adsorption of the D8/MA might be considered lower than expected, due to the significant lower molecular weight of this co-oligomer relative to the other oligomer treatment. It was also observed that the amount of dispersant adsorbed did not vary over a 0-10⁻⁴M NaCl salinity gradient.

Isomeric oxides (i.e., aluminum, silicon, and zirconium) can be deposited as separate entities or as mixed oxides on TiO₂. The oxide layers may be deposited at variable density levels by proprietary processes. The matrix of inorganic oxide layers deposited varied in Table 3. The individual metal oxide inorganic points (IEPs) are: 9.0 for Al₂O₃-7, 5.6 for ZrO₂, and 7.2 for TiO₂. One of the Al₂O₃-7 samples exhibited a lower IEP of 5.6. Sample 3, Al₂O₃-7 (3.6 wt%) is co-precipitated with SiO₂ (6.5 wt%).

In sample 3, three layers were deposited in separate stages with SiO₂ deposited at 6.0 wt%, only, as the first layer. A layer of Al₂O₃ was then deposited (ca. 2.0 wt%), followed by a third layer of ZrO₂ (1.25 wt%). The Al₂O₃ layer reacts with the SiO₂ to lower the metal oxide-treated TiO₂ grind. With a greater number of unneutralized acids to hydrogen bond or acid-base interact with the surface of TiO₂ whereas, in sample 5, the IEP indicates that Al₂O₃ is the primary surface component. In sample 6, although Al₂O₃ is applied in an equal amount to Al₂O₃ (1 wt%), the IEP indicates that the surface is primarily Al₂O₃. It might be expected that at a pH of 9.3, the higher IEP surfaces with remaining hydroxy groups could more readily participate in reverse hydrogen bonding or acid-base interaction with the maleic acid dispersant, also not fully ionized, and this would promote greater adsorption. Adsorption of the two model dispersants, [CH₃(CH₂)₄]_4/MA and [CH₃(CH₂)₄]₄/MA from a dispersion medium of pH 9.3 (figures 4a and 4b) parallel the substrate IEP values of the treated TiO₂. The adsorption of the surfactant, or again less than the [CH₃(CH₂)₄]₄/MA, but the dependence on the metal oxide IEP is observed.

Table 3—Characteristics of Different Surface-Treated TiO₂ Pigments

<table>
<thead>
<tr>
<th>Sample #</th>
<th>IEP (pH)</th>
<th>Surface Area (m²/g)</th>
<th>Description of TiO₂ Pigments (Surface Concentration wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.0</td>
<td>15</td>
<td>4.5 Al₂O₃ / TiO₂</td>
</tr>
<tr>
<td>2</td>
<td>6.3</td>
<td>15</td>
<td>3.6 Al₂O₃ / TiO₂</td>
</tr>
<tr>
<td>3</td>
<td>4.51</td>
<td>12.2</td>
<td>1.25 ZrO₂ / 2.0 Al₂O₃ / 10 SiO₂</td>
</tr>
<tr>
<td>4</td>
<td>6.36</td>
<td>14.7</td>
<td>2.0 Al₂O₃ / TiO₂ / 23 SiO₂</td>
</tr>
<tr>
<td>5</td>
<td>8.25</td>
<td>15.0</td>
<td>1.10 ZrO₂ / 1.0 Al₂O₃</td>
</tr>
</tbody>
</table>

(1) Surface concentration of inorganic oxides is described according to the order of surface treatment as noted.

Aluminum oxide treatment of the TiO₂ surface is the most common commercial type, so the adsorption behavior of maleic acid co-oligomers on Al₂O₃-treated TiO₂ will be examined first. Three types of maleic acid dispersants were used. The [CH₃(CH₂)₄]₄ maleic acid (hereafter referred to as D8/MA) dispersant adsorbs more than the smaller α-olefin [(CH₂)₇(CH₄)₄] maleic acid (D4/MA) while the adsorption of the styrene-co-oligomer (Table 1) is very low from 9.3 pH dispersions (figure 3). The dispersants vary in the size of the pendant hydrocarbon group and the number of double bonds in the main chain. These groups in the early decades of surface chemistry have been approximated as 2.5 carbons based on its surface activity. Using this criterion, the adsorption behavior of the dispersants on Al₂O₃-treated TiO₂ is determined by the hydrophobe size of the dispersant. This would consist of Al₂O₃-7 for ZrO₂ and Al₂O₃-8 for the other oligomer treated with the smaller α-olefinic acid. This is consistent with a medium of lower dielectric constant to the contiguous acid. This complemented by the repulsion of two contiguous anionic groups in maleic acid salts, facilitates maintenance of half of the carboxylate groups as unionized acids, even at a dispersion pH of 9.3.

Molecular weight also is an important parameter in the adsorption process. The adsorption of the D8/MA might be considered lower than expected, due to the significant lower molecular weight of this co-oligomer relative to the other oligomer treatment. It was also observed that the amount of dispersant adsorbed did not vary over a 0-10⁻⁴M NaCl salinity gradient.

Isomeric oxides (i.e., aluminum, silicon, and zirconium) can be deposited as separate entities or as mixed oxides on TiO₂. The oxide layers may be deposited at variable density levels by proprietary processes. The matrix of inorganic oxide layers deposited varied in Table 3. The individual metal oxide inorganic points (IEPs) are: 9.0 for Al₂O₃-7, 5.6 for ZrO₂, and 7.2 for TiO₂. One of the Al₂O₃-7 samples exhibited a lower IEP of 5.6. Sample 3, Al₂O₃-7 (3.6 wt%) is co-precipitated with SiO₂ (6.5 wt%).

In sample 3, three layers were deposited in separate stages with SiO₂ deposited at 6.0 wt%, only, as the first layer. A layer of Al₂O₃ was then deposited (ca. 2.0 wt%), followed by a third layer of ZrO₂ (1.25 wt%). The Al₂O₃ layer reacts with the SiO₂ to lower the metal oxide-treated TiO₂ grind. With a greater number of unneutralized acids to hydrogen bond or acid-base interact with the surface of TiO₂ whereas, in sample 5, the IEP indicates that Al₂O₃ is the primary surface component. In sample 6, although Al₂O₃ is applied in an equal amount to Al₂O₃ (1 wt%), the IEP indicates that the surface is primarily Al₂O₃. It might be expected that at a pH of 9.3, the higher IEP surfaces with remaining hydroxy groups could more readily participate in reverse hydrogen bonding or acid-base interaction with the maleic acid dispersant, also not fully ionized, and this would promote greater adsorption. Adsorption of the two model dispersants, [CH₃(CH₂)₄]_4/MA and [CH₃(CH₂)₄]₄/MA from a dispersion medium of pH 9.3 (figures 4a and 4b) parallel the substrate IEP values of the treated TiO₂. The adsorption of the surfactant, or again less than the [CH₃(CH₂)₄]₄/MA, but the dependence on the metal oxide IEP is observed.

The amount of surfactant adsorbed was quantified by two techniques: SEC and UV absorbance of the lower surfactant in the aqueous phase; the adsorption studies were conducted in the aqueous phase at pH 7.5. The UV absorbance data reflects a slightly greater adsorption than the SEC data. Preferential adsorption of the lower ethoxylates would be expected. This would remove a greater percentage of the aromatic rings, the detection site in the UV analysis. The aromatic ring is not the quantifying parameter in the SEC analysis. In this study, the pH of the aqueous dispersion was raised only to 7.5 value, parallelizing an interior latex coating. When the smaller α-olefin/MA dispersant is used, there is a notable difference between the surfactant and adsorption on Al₂O₃-treated TiO₂ relative to the substrate with an excess of SiO₂ treatment. With the small pigment group (D4/MA), the [CH₃(CH₂)₄/MA] dispersant adsorbs significantly less than the D8/MA dispersant; there is little to attract the nonionic surfactant to even the Al₂O₃/TiO₂ interface. But there is an exception with pigment 2, containing an excess of SiO₂. The amount of surfactant absorbed increases with SiO₂ treatment. The surfactant adsorption data (discussed later) are close to sample 1, which was treated with only Al₂O₃.

**Competitive Adsorption of HEUR Thickeners**

In these experiments, TiO₂ has been sequentially pre-treated with Al₂O₃ sample 1) or other mixed inorganic oxide (Table 3), then with an organic oligomeric dispersant, D4/MA or D8/MA, at a 0.3 g dispersant per 100 g of TiO₂ level, and finally with a nonionic surfactant, CH₃(CH₂)₇(CH₃)₄OCH₂CH₃ (CH₃(CH₂)₄EO₄)(H₂O)₄, at 0.8 wt%, a significant excess. This sequence would be the practice in preparing a pigment grind for a waterborne coating formulation. The HEURs varied in terminal hydrophobe size connected with the EO chain by a large disiocyanate, methylene bis-4(3)-
The chromatography system consisted of a Waters 510 HPLC pump, a Waters 6676 injector with a 2 ml loading loop, a Waters R401 differential refractometer, a Waters 730 data module, a mobile phase of HPLC grade tetrahydrofuran, a flow rate of 1.0 ml/min, a column temperature of 30°C, an injection volume of 200 ml, and a Shodex KF-802 (upper exclusion limit 5,000 Daltons) size exclusion column. The refractive index difference between the reference and sample cell was used to analyze the adsorption isotherms, and all analyses were performed in the HPLC mode with a peak limit. Calibration curves were prepared using aqueous surfactant and thicker solutions between 0.1 and 1.0 wt%.

RESULTS AND DISCUSSION

Structural Influence of the Organic Oligomeric Acid and Metal Oxide Treatment on Adsorption

Titanium dioxide reacts with organic materials by electron transfer from the substrate to the electron-deficient group. This type of degradation, it is common practice for the manufacturers to pretreat TiO₂ with either Al₂O₃ or SiO₂, or both. These parameters are examined using model pHUR thickeners. It is also a common practice to add an organic dispersant (e.g., an acrylic or methacrylic acid oligomer or an olefin/maleic acid copolymer) to lower the metal oxide-treated TiO₂ grind. With a greater number of unneutralized acids to hydrogen bond or acid-base interact with the pigment surface, the maleic acid co-oligomer adsorbs significantly more than the oligomeric methacrylic acid dispersant. The co-oligomer also possesses hydrophobic units to interact and 'adhere' to the conventional surfactant and associative thickeners on the TiO₂ surface.

Aluminum oxide treatment of the TiO₂ surface is the most common commercial type, so the adsorption behavior of maleic acid co-oligomers on Al₂O₃-treated TiO₂ will be examined first. Three types of maleic acid dispersants were used. The (CH₂=CH-COOH)₃ maleic acid (hereafter referred to as D8/MA) dispersant adsors more than the smaller (CH₂=CH(CH₂)₄ maleic acid (D4/MA) while the adsorption of the styrene-co-oligomer (Table 3) is very low from 9.3 pH dispersions (Figure 3). The dispersants vary in the size of the pendant hydrocarbon group and the metallic oxide type of the main group. In the early decades of surface chemistry has been approximated as 2.5 carbons based on its surface activity. Using this criterion, the adsorption behavior of the dispersants on Al₂O₃-treated TiO₂ is determined by the hydrophobe size of the dispersant. This would be consistent with Al₂O₃-6.7 for ZrO₂ and Al₂O₃-9.4 for ZrO₂-1.0, a medium of lower dielectric constant to the conjugated acid. It is complemented by the repulsion of two con-tiguous anionic groups in maleic acid salts, facilitates maintenance of half of the carboxylate groups as unionized acids, even at a dispersion pH of 9.3.

Molecular weight also an important parameter in the adsorption process. The adsorption of the D8/MA might be considered lower than expected, due to the significantly lower molecular weight of this co-oligomer relative to the other-oligomer present in this study. It was also observed that the amount of dispersant adsorbed did not vary over a 0 to 10⁻⁵ M NaCl salinity gradient.

Isomeric oxides (i.e., aluminum, silicon, and zirconium) can be deposited as 15⁺ or as mixed oxides on TiO₂. The oxide layers may be deposited as variable density layers by proprietary layer-by-layer techniques. The matrix of inorganic oxide layers deposited was listed in Table 3. The individual metal oxide isoelectric points are: IEP= 9 for Al₂O₃; 5.7 for ZrO₂, and 4.8 for SiO₂. In sample 1, only Al₂O₃ is deposited at 4.5 wt%. In sample 2, Al₂O₃ (3.6 wt%) is co-deposited with SiO₂ (6.5 wt%).

In sample 3, three layers were deposited in separate stages with SiO₂ deposited (at 6.0 wt%), only as the first layer. A layer of Al₂O₃ was then deposited (ca. 2.0 wt%), followed by a third layer of ZrO₂ (1.25 wt%). The individual metal oxide points for sample 1 are listed in Table 3. These values appear to be dominated by the surfacem. In sample 3, relative to the others’ samples studied. Based on the isoelectric points, the surface chemistry of sample 3 is seen to be dominated by SiO₂ and ZrO₂. In samples 4 and 5, there are only two inorganic oxide treatments. In sample 4, the first layer consists of a mixture of SiO₂ (0.4 wt%) and ZrO₂ (7.2 wt%). A mixed layer of ZrO₂ (0.4 wt%) and Al₂O₃ (6.7 wt%) is applied first in sample 5. The second layer applied to both samples 4 and 5 is Al₂O₃ (5.6 wt%). The lower surface area of sample 3 relative to the other samples studied. Based on the isoelectric points, the surface chemistry of sample 3 is seen to be dominated by SiO₂ and ZrO₂. In samples 4 and 5, there are only two inorganic oxide treatments. In sample 4, the first layer consists of a mixture of SiO₂ (0.4 wt%) and ZrO₂ (7.2 wt%). A mixed layer of ZrO₂ (0.4 wt%) and Al₂O₃ (6.7 wt%) is applied first in sample 5. The second layer applied to both samples 4 and 5 is Al₂O₃ (5.6 wt%). The lower surface area of sample 3 relative to the other samples studied.

Table 3—Characteristics of Different Surface-Treated TiO₂ Pigments

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Isoelectric Point (IEP)</th>
<th>Surface Area</th>
<th>Description of TiO₂ Pigments</th>
<th>Surface Concentration (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.0</td>
<td>15</td>
<td>4.5 Al₂O₃ / TiO₂</td>
<td>9.1 Al₂O₃ / TiO₂</td>
</tr>
<tr>
<td>2</td>
<td>6.3</td>
<td>15</td>
<td>3.6 Al₂O₃ / TiO₂</td>
<td>9.1 Al₂O₃ / TiO₂</td>
</tr>
<tr>
<td>3</td>
<td>4.51</td>
<td>12.2</td>
<td>1.25 ZrO₂ / 2.0 Al₂O₃ / 6.0 SiO₂</td>
<td>9.1 Al₂O₃ / TiO₂</td>
</tr>
<tr>
<td>4</td>
<td>4.30</td>
<td>14.7</td>
<td>2.0 Al₂O₃ / 1.0 ZrO₂ / 3.0 SiO₂</td>
<td>9.1 Al₂O₃ / TiO₂</td>
</tr>
<tr>
<td>5</td>
<td>8.28</td>
<td>15.8</td>
<td>2.0 Al₂O₃ / 1.0 ZrO₂ / 3.0 SiO₂</td>
<td>9.1 Al₂O₃ / TiO₂</td>
</tr>
</tbody>
</table>

(15) Surface concentration of ionic species is described according to the order of surface treatment as listed.

Adsorptive Thicker Influences on Waterborne Coatings: II

Figure 4—Adsorption of α-olefin/maleic acid co-oligomer dispersants (D8/MA) on titanium dioxide pigments surface-treated with mixed inorganic oxides. Symbols: (a) sample 5, (b) sample 6, (c) sample 4, and (d) sample 3.

Figure 5—Adsorption (UV analysis) of nonionic surfactant C10₂H₂₁-C₄H₉(OEO)₄H on TiO₂ pre-treated with co-oligomer dispersants and metal oxide. Symbols: (a) sample 5, (b) sample 6, (c) sample 4, and (d) sample 3. Closed symbol: C8, open symbol: D4. Closed symbols indicate the sample was open symbol: MA, open symbol: MA/dispersion.

Figure 6—Adsorption (UV analysis) of nonionic surfactant C10₂H₂₁-C₄H₉(OEO)₄H on TiO₂ pre-treated with co-oligomer dispersants and metal oxide. Symbols: (a) sample 5, (b) sample 6, (c) sample 4, and (d) sample 3. Closed symbol: C8, open symbol: D4. Closed symbols indicate the sample was open symbol: MA, open symbol: MA/dispersion.

Figure 7—Adsorption (UV analysis) of nonionic surfactant C10₂H₂₁-C₄H₉(OEO)₄H on TiO₂ pre-treated with co-oligomer dispersants and metal oxide. Symbols: (a) sample 5, (b) sample 6, (c) sample 4, and (d) sample 3. Closed symbol: C8, open symbol: D4. Closed symbols indicate the sample was open symbol: MA, open symbol: MA/dispersion.

Figure 8—Adsorption of α-olefin/maleic acid co-oligomer dispersants (D8/MA) on titanium dioxide pigments surface-treated with mixed inorganic oxides. Symbols: (a) sample 5, (b) sample 6, (c) sample 4, and (d) sample 3.

Competitive Adsorption of HEUR Thickeners

In these experiments, TiO₂ had been sequentially pre-treated with Al₂O₃ sample 1 or other mixed inorganic ones (Table 3), then with an organic oligomeric dispersant, D4/MA or D8/MA, at a 0.3 g/L dispersion per 100 g of TiO₂ level, followed by a nonionic surfactant, C₄H₉₋₅C₆H₄(OEO)₄H, at 0.8 wt%, a significant excess. This sequence would be the practice in preparing a pigment grind for a waterborne coating formulation. The HEURs varied in terminal hydroxide size connected with the EO chain by a large disiocyanate, methylene bis- 4(3)-
cyclohexyl disiocyanate (HMDI) units, at the E0 terminal positions. A generalized structure for the model unHiERs, with narrow molecular weight distributions, is provided in Scheme 1. The use of narrow molecular weight HEUR thickeners in the adsorption study is important for they are the only type of HEUR thickener with a well-defined structure and a high degree of hydrophobic modification (>95%). Broad molecular weight model S-G-HEURs are also studied.

The strength of hydrophobic interaction time in hydrophobic associations increase with increasing terminal hydrophobic size, and the viscosity increases with increasing terminal hydrophobic groups. With those studies, the larger terminal sizes in this HEUR series were more effective in displacing the formulation surfactant, C12H25CH2CH2OH (0.1 M) from the (polyacrylic acid) latex surfaces. Consistent with the need for a hydrophobic interaction, less HEUR is adsorbed on TiO2 pretreated with the smaller MA/DA dispersed (Figure 6a).

However, the dramatic adsorption differences noted among different terminal hydrophobic sizes in the latex studies are evident in either the narrow molecular weight (Figure 6a) or Step-Growth (Figure 6b) HEURs in the TiO2 adsorption studies. As expected, there is greater adsorption with the narrow molecular weight unHiERs than with the S-G HEURs because of the relative purity of the former thickener.

The effect of the metal oxide treatment of the TiO2 surface on the ultimate adsorption of a C12H25(CH2CH2OH)n, (n=1-4) polyacrylic acid (PAA) latex is shown in Figure 7. The HEUR surfactant is the IEP of the pigment's surface when the organic dispersant D/M/A is adsorbed on the oxide surface. When TiO2 is pretreated with D/M/A dispersant, the adsorption of unHiERs on pigments is very low.

Surface Displacement

In a prior study, a series of very large hydrophobe, model organic dispersants (the C12H25, C12H25CH2OH, and C12H25C6H4OH α-olefinic co-oligomers with maleic acid, sodium salt) were adsorbed onto a Al2O3 pretreated TiO2. The individual formulation surfactant, C12H25CH2CH2OH (0.1 M), and two model HEURs were studied. The adsorptions of both the formulation surfactant and the model HEURs were determined, independently, by an iodine absorbance method (UV analysis) for oxochlorane units. However, the competitive adsorption of the HEURs in the presence of the nonionic surfactant could not be measured by this TOE/iodine UV absorbance, due to their close similarity in UV absorbance characteristics.

The surfactant, C12H25CH2CH2OH (0.1 M), concentration used in this study is 0.8 wt%, well into the adsorption plateau region, based on the data in Figure 5. The available adsorption sites for the surfactant on the TiO2 should be occupied. The hydrophobes of the HEURs would be expected to displace the surfactant, as was observed in a previous latex study. However, for the large terminal hydrophobic of the HEURs, the more efficient it would be. In reality, when the H2MDI-HEURs were adsorbed (SEC technique), the adsorption nonionic surfactant (UV analysis of the free solution concentrations) did not desorb significantly from the metal oxide/TiO2 surface (Figures 7 and 8) pretreated with the larger D/M/A dispersant; however, this is not observed when the smaller D/M/A is added to the metal oxide/TiO2 dispersion, and the dispersion pH is 7.5, as it might be with an interior coating formulation. Very little, if any, surfactant is associated with the Al2O3 pretreated TiO2 dispersion; however, there is a significant amount of association in the presence of HEUR thickeners when the metal oxide treatment is S-G.

CONCLUSIONS

The metal oxide treatment of the TiO2 surface influences the amount of dispersant adsorbed. In adsorption from pH 5.9 aqueous media, the amount of adsorption increases as the isoelectric point of the metal oxide-treated TiO2 increases. It would be expected that at a pH of 9.3 the hydrophobes would more readily participate in a hydrogen bonding or acid-base interaction with maleic acid co-oligomer dispersants that have high pHex, and this would promote greater adsorption. The size of the oligomer pendant group also influences the amount of associative Thickener Influences on Waterborne Coatings: II maleic acid co-oligomer adsorbed, and it is observed that adsorption of the C12H25-co-oligomer is lower and less sensitive in its adsorption to different inorganic oxide treatments of TiO2 to a C12H25C6H4OH α-olefinic co-oligomer. Within this matrix, when the metal oxide on the TiO2 surface is Al2O3, the nonionic surfactant does not adsorb significantly on pigments pretreated with the smaller organic dispersant with pendant C12H25 units. The surfactant does adsorb on the smaller dispersant-treated TiO2 when the metal oxide is primarily SiO2, and the pH of the aqueous media is decreased to 7.5. Only in this latter case is there evidence that the nonionic surfactant is displaced with adsorption of the HEUR thickener. With the larger pendant C12H25—dispersed on the Al2O3-treated TiO2, the nonionic surfactant is not displaced by the adsorbing HEUR thickener.

References

cyclohexyl diisocyanate (H₂MDI) units, at the EO terminal positions. A generalized structure for the model unimer HEURs, with narrow molecular weight distributions, is provided in Scheme 1. The use of narrow molecular weight HEUR thickeners in the adsorption study is important for they are the only type of HEUR thickener with a well-defined structure and a high degree of hydrophobic modification (29%). Broad molecular weight model S-G HEURs are also studied.

The strength of terminal moieties in hydrophobic associates increases with increasing terminal hydrophobic size, and the viscosity increases with increasing terminal hydrophobic size. With these studies, the largest terminal sizes in this HEUR series were more effective in displacing the formulation surfactant, C₂₃H₄₇COOH, from the polymeric (polyacrylate) latex surfaces. Consistent with the need for a hydrophobic interaction, less HEUR is adsorbed on TiO₂-prettreated with the smaller MA/DMA dispersant (Figure 6a). However, the dramatic adsorption differences noted among different terminal hydrophobe sizes in the latex studies are evident in either the narrow molecular weight adsorption (Figure 6a) or Steep-Growth (Figure 6b) HEURs in the TiO₂ adsorption studies. As expected, there is greater adsorption with the narrow molecular weight unimer HEURs than with the S-G HEURs because of the relative purity of the former thickener.

The effect of the metal oxide treatment of the TiO₂ surface on the ultimate adsorption of a C₃₅H₇₀díMDI (EO:x =H₂MDI)=C₃₂H₆₆COOH unimer HEUR thickener follows the IEP of the pigment's surface when the organic dispersant DMA/MA is adsorbed on the oxide surface. When TiO₂ is pretreated with DMA/MA dispersant, the adsorption of unimer HEURs on pigments is very low.

Surfactant Displacement

In a prior study, a series of very large hydrophobe, model organic dispersants (the C₃₅H₇₀díMDI, DMA/MA, and C₆₈H₁₃₅O₂ Aluminum acid co-oligomers with maleic acid, sodium salt) were adsorbed onto a Al₂O₃-prettreated TiO₂. The individual formulation surfactant, C₂₃H₄₇COOH, was added separately, and several commercial HEURs also were studied. The adsorptions of both the formulation surfactant and the model HEURs were determined, independently, by an iodine absorbance method (UV analysis) for oleylamine units. However, the competitive adsorption of HEURs in the presence of the nonionic surfactant could not be measured by this POE/iodine UV absorbance, due to their close similarity in structure.

The surfactant, C₂₃H₄₇COOH HEUR concentration used in this study is 0.8 wt%, well into the adsorption plateau region, based on the data in Figure 5. The available adsorption sites for the surfactant on the pretreated TiO₂ should be occupied. The hydrophobes of the HEURs would be expected to displace the surfactant, as was observed in a previous latex study; the larger the effective terminal hydrophobe of the HEURs, the more efficient it would be. In reality, when the H₂MDI-HEURs were adsorbed (SEC technique), the formulation nonionic surfactant UV analysis of the free solution concentrations did not desorb significantly from the metal oxide/TiO₂ surface (Figures 7 and 8) pretreated with the larger DMA/MA dispersant; however, this is not observed when the smaller DMA/MA is added to the metal oxide/TiO₂ dispersant, and the dispersion pH is 7.5, as it might be with an interior coating formulation. Very little, if any, surfactant is associated with the Al₂O₃ pre-tiO₂ dispersed; however, there is a significant amount of association in the presence of HEUR thickeners when the metal oxide treatment is SiO₂.

CONCLUSIONS

The metal oxide treatment of the TiO₂ surface influences the amount of dispersant adsorbed. In adsorption from pH 9.5 aqueous media, the amount of adsorption increases as the isoelectric point of the metal oxide-treated TiO₂ increases. It would be expected that at a pH of 9.3 the hydroxide could more readily participate in a hydrogen bonding or acid-base interaction with maleic acid co-oligomer dispersants that have high pKₐ, and this would promote greater adsorption. The size of the co-oligomer pendant group also influences the amount of

References

(3) Ma, C., Colloids and Surfaces, 16, 185 (1993).
(9) Kuo, C., Provider, T., and Kah, A.E., Print Rev. & Print, April 1983.