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

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Size exclusion chromatography in tandem with UV absorbance of the surfactant is used to separate and quantify the amount of nonionic surfactant and model hydrophobically modified ethoxylated urethane (HEUR) thickeners adsorbed on different organic oligomeric polyacid, metal oxide-treated TiO_2 surfaces. The isoelectric point imposed on TiO_2 by the metal oxide surface treatment determines the amount of organic dispersant adsorbed. The size of the α-olefin on the maleic acid dispersant is also important in the adsorption of the dispersant. The size of the α-olefin on the organic acid dispersant, in turn, determines the amount of surfactant and HEUR thickener adsorbed. The surfactant, unlike the HEUR thickener, exhibits a dependence on the metal oxide treatment in neutral media, independent in several aspects of the amount of organic dispersant adsorbed. The adsorption dependence of HEUR thickeners and nonionic surfactant on the hydrophobe size of the HEUR is discussed.

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[1] considerations. It has been observed in the competitive adsorptions of sodium dodecylsulfate (SDS) and ethoxylated nonylphenol[2] (NP–$(EO)_{12}$H) blends[3] on TiO_2 that NP$(EO)_{12}$H alone is not adsorbed significantly on TiO_2; however, the amount of NP–$(EO)_{12}$H adsorbed increased by more than 50 times in the presence of lower amounts of SDS, but decreases at higher SDS concentrations. Adsorption on TiO_2 is reported to be affected by the order of addition,[4] in 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 hiding 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 disperse phase, it is treated with surfactant and an oligomeric polyacid dispersant. The adsorption of surfactant and dispersant increases the stability of the dispersion by increasing the electrosteric repulsion between particles,[5] but in the presence of a nonadsorbing thickener, the stability of the TiO_2 is often not stable enough to ensure good applied film gloss.

In Part I of this series,[6] the interactions among model hydrophobically modified ethoxylated urethane (HEUR) thickeners and a surfactant-free 123 nm acrylic latex were studied. In those experiments, three different surfactants (of the type used in waterborne latex coatings) were added, separately, with model HEURs to the latex dispersion. 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 (Al_2O_3, ZrO_2, and SiO_2) treatment of TiO_2 on the adsorption of the oligomeric polyacid dispersant when the chemical composition of alpha-olefin/maleic acid co-oligomers are changed. These changes are then quantified for their influence on the amounts of

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model HEUR associative thickeners and nonionic surfactant adsorbed under competitive conditions on the pretreated TiO_2. Analysis of 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. Step-growth (S-G) HEUR[7] thickeners, that also will be studied, have a broad molecular weight distribution that encompasses unreacted poly(oxyethylene) (POE) starting material.[8] The surfactant is very low in molecular weight; and the one used in this study, $CH_3C(CH_3)_2–CH_2–C(CH_3)_2–C_6H_4–O–(CH_2CH_2O)_{10}H$ (referred to as $C_8H_{17}–C_6H_4O(EO)_{10}H$ in the rest of this article), has a molecular weight average of 646.96. This average encompasses 11 different components.[9] Thus, both surfactants and thickeners contained a multitude of molecular weight components.

In a prior study,[10] 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 thickener and surfactant can be realized.

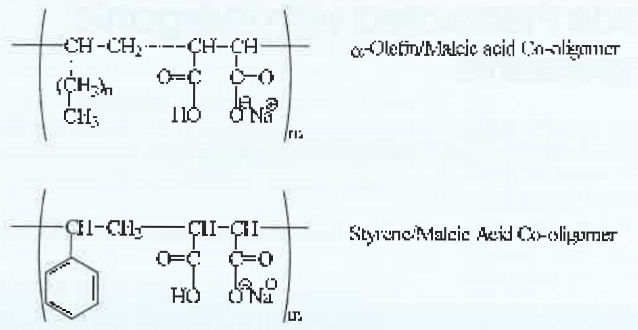
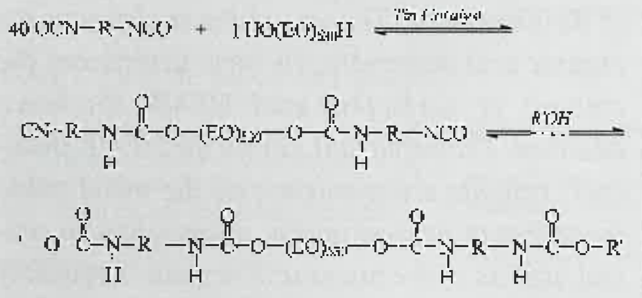


Figure 1—General structures of styrene/maleic acid and α-olefin/maleic acid model dispersants. n = 3 or 7, referred to as D4 and D8.

Table 1—Molecular Weights of Alpha-Olefin/Maleic Acid (C_xH_{2x}/Maleic Acid) Dispersants by Size Exclusion Chromatography

Dispersant	M_n	M_w	PDI
$C_{10}H_{20}$/MAcid	1520	2600	1.7
C_6H_{12}/MAcid	3450	8190	2.4
Styrene/MAcid	4400	9300	2.1



Scheme 1—Synthesis of model narrow molecular weight distribution hydrophobe-modified ethoxylated urethane (uniHEUR) thickeners.

Table 2—Molecular Weights of R'-NH-CO-NH-C_6H_{10}-CH_2-C_6H_{10}-(NH-CO-O-$(CH_2CH_2O)_{198}$-CO-NH-C_6H_{10}-CH_2-C_6H_{10}-)$_3$ NH-CO-NH-R' HEUR Associative Thickeners by Size Exclusion Chromatography

R'=S-G; R*=UniHEURS	M_n	M_w	PDI
R' = C_8H_{17}	24,200	34,600	1.4
R' = $C_{12}H_{25}$	22,100	34,300	1.4
R* = C_8H_{17}	33,400	37,200	1.1
R* = $C_{12}H_{25}$	32,100	35,700	1.1

R* = uniHEURs structure given in Scheme I.

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 α-olefins were hexene and decene. 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.[11] The surfactant, $C_8H_{17}–C_6H_4O(EO)_{10}H$ (an ethoxylated octylphenol with an average of 9-10 oxyethylene units) was obtained from Union Carbide. The synthesis, characterization, and isolation of the model uniHEURs and step-growth HEURs (*Scheme* 1) have been described[7,8]; 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 broad molecular weight distribution of 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 DDI water and rolling the solutions for 48 hr. 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).

Adsorption Studies

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 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 carboxylate anions and is not soluble in organic solvents. The dispersants also were likely to adsorb irreversibly[12] on the SEC column.

The SEC technique was used to measure the adsorption of the nonionic surfactant, C_8H_{17}–$C_6H_4O(EO)_{10}H$, on titanium dioxide stabilized by hydrophobic dispersants. Surfactant adsorption also was measured by UV spectroscopy. The SEC technique monitored the peak area at 7.35 minutes elution time for C_8H_{17}–$C_6H_4O(EO)_{10}H$; 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 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 adsorptions, 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. Equilibria in the competitive adsorption studies were reached by rolling dispersions with all components for 24 hr. The pigment dispersions were centrifuged with a DuPont Sorvall (RC-5B) refrigerated superspeed centrifuge at 3°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 varience was ±3%.

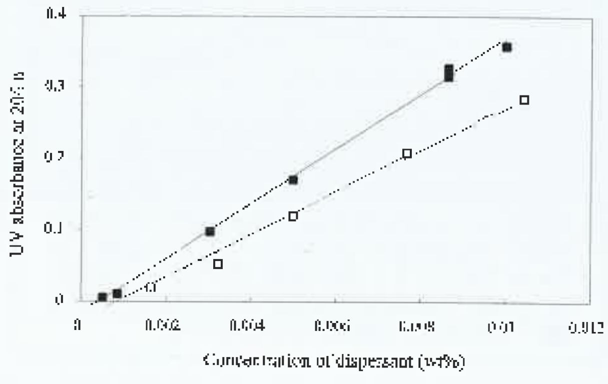


Figure 2a—Calibration curve of dispersants by UV absorbance at 204 nm with different dispersant concentration. Symbols: (□)—C_6H_{12}/MAcid; (■)—$C_{18}H_{36}$/MAcid.

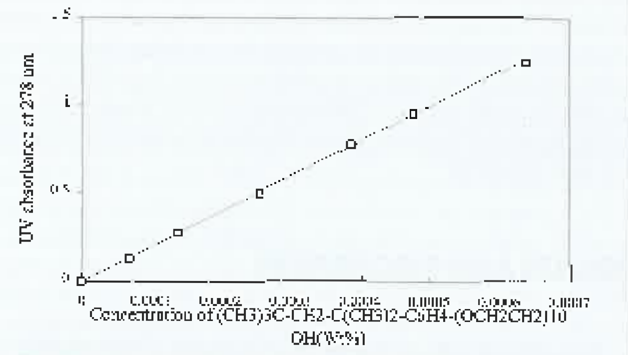


Figure 2b—Calibration curve of $(CH_3)_3C–CH_2–C(CH_3)_2\ C_6H_4–(OCH_2CH_2)_{10}–OH$ nonionic surfactant by UV absorbance at 278 nm with different concentration diluted with 50/50 weight ratio mixture of water/methanol solution.

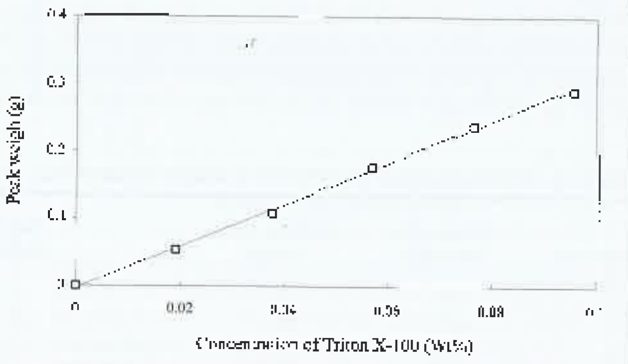


Figure 2c—Calibration curve of $(CH_3)_3C–CH_2–C(CH_3)_2–C_6H_4–(OCH_2CH_2)_{10}–OH$ nonionic surfactant by SEC elution time at 7.20 min.

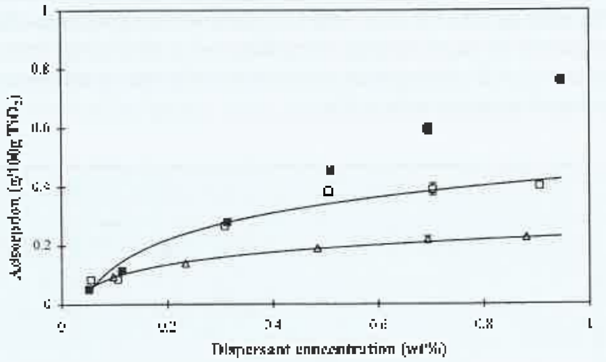


Figure 3—Adsorption of maleic acid co-oligomeric dispersants on Al_2O_3/TiO_2 (sample 1 in Table 3) at pH 9.3. Symbols: (Δ) styrene/maleic acid, (□) 1-hexene/maleic acid (D4/MA), and (■) 1 decene/maleic acid (D8/MA).

The chromatography system consisted of a Waters 510 HPLC pump, a Waters U6/K 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 adsorptions, and all analyses were performed in the HPLC mode to obtain peak areas. Calibration curves were prepared using aqueous surfactant and thickener solutions between 0.1 and 1.0 wt%.

RESULTS AND DISCUSSION

Structural Influence of the Organic Oligomeric Acid and Metal OxideTreatment on Adsorption

Titanium dioxide reacts with organic materials by electron transfer reactions. To protect the binder from this type of degradation, it is a common practice for the manufacturer to pretreat TiO_2 with either Al_2O_3 or SiO_2, or both. These parameters are examined using model HEUR thickeners. 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 co-oligomer) to the metal oxide-treated TiO_2 grind. With a greater number of unneutralized acids to hydrogen bond or acid-base interact with the pigment surface,[1] the maleic acid co-oligomer adsorbs significantly more than the oligomeric methacrylic acid dispersant. The co-oligomer also possesses hydrophobic units to interact and "adsorb" the conventional surfactant and associative thickeners on the TiO_2 surface.

Aluminum oxide treatment of the TiO_2 surface is the most common commercial type, so the adsorption behavior of maleic acid co-oligomers on Al_2O_3 treated TiO_2 will be examined first. Three types of maleic acid dispersants were used. The $[CH_2CH(C_8H_{17})/\text{maleic acid}]$ (hereafter referred to as D8/MA) dispersant adsorbs more than the smaller α-olefin $[CH_2CH(C_4H_9)/\text{maleic acid}]$ (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 molecular weight of the co-oligomers. The phenyl 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 Al_2O_3-treated TiO_2 is determined by the hydrophobe size of the dispersant. This would be consistent with the prior observation that the α-olefin promotes a medium of lower dielectric constant to the contiguous acid.[13,14] 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 significantly lower molecular weight of this co-oligomer relative to the other co-oligomer group in this study. It was also observed that the amount of dispersant adsorbed did not vary over a 0 to 10^{-2} M NaCl salinity gradient.

Inorganic oxides (i.e., aluminum, silicon, and zirconium) can be deposited[15-17] as separate entities or as mixed oxides on TiO_2. The oxide layers may be deposited at variable density levels by proprietary processes. The matrix of inorganic oxide layers deposited is listed in *Table* 3. The individual metal oxide isoelectric points (IEP) are: 9 for Al_2O_3, 6-7 for ZrO_2, and 3-4 for SiO_2. In sample 1, only Al_2O_3 is deposited at 4.5 wt%. In sample 2, Al_2O_3 (3.6 wt%) is co-precipitated with SiO_2 (6.5 wt%).

In sample 3, three layers were deposited in separate stages with SiO_2 deposited (at ca. 6.0 wt%), only, as the first layer. A layer of Al_2O_3 was then deposited (ca. 2.0 wt%), followed by a third layer of ZrO_2 (1.25 wt%). The excess amount of SiO_2 deposited appears to lower the surface area of sample 3 relative to the other samples studied. Based on the isoelectric points, the surface chemistries in sample 3 appear to be dominated by SiO_2 and ZrO_2. In samples 4 and 5, there are only two inorganic oxide treatments. In sample 4, the first layer consists of a mixture of ZrO_2 (0.4 wt%) and SiO_2 (2 wt%). A mixed layer of ZrO_2 (0.4 wt%) and Al_2O_3 (1 wt%) is applied first in sample 5. The second layer applied to both samples 4 and 5 is Al_2O_3 (2 wt%). The lower IEP in sample 4 probably indicates the significant presence of all three oxides on

Table 3—Characteristics of Different Surface-Treated TiO_2 Pigments[a]

Sample #	Isoelectric Point (IEP)	Surface Area (m^2/g)	Description of TiO_2 Pigments (Surface Concentration wt%)
1	9.0	15	4.5 Al_2O_3 | TiO_2
2	6.3	15	3.6 Al_2O_3 – 6.5 SiO_2 | TiO_2
3	4.51	12.2	1.25 ZrO_2 | 2.0 Al_2O_3 | 6.0 SiO_2 | TiO_2
4	6.36	14.3	2.0 Al_2O_3 | 0.5 ZrO_2–2.0 SiO_2 | TiO_2
5	8.49	14.1	2.0 Al_2O_3 | 0.5 ZrO_2–1.0 Al_2O_3 | TiO_2
6	8.28	15.0	1.0 ZrO_2–1.0 Al_2O_3 | TiO_2

(a) Surface composition of inorganic oxides is described according to the order of surface treatment, see text.

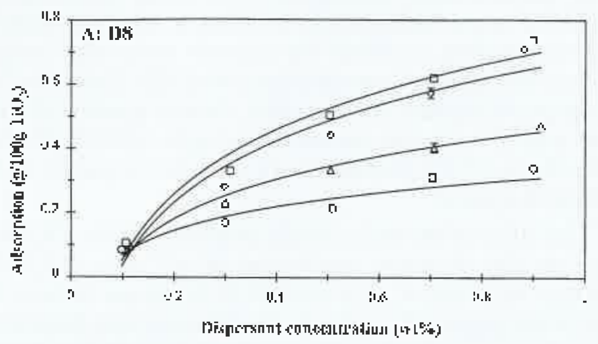


Figure 4a—Adsorption of α-olefin/maleic acid co-oligomer dispersants (D8/MA) on titanium dioxide pigments surface treated with mixed inorganic oxides. Symbols: (□) sample 5, (◇) sample 6, (Δ) sample 4, and (○) sample 3.

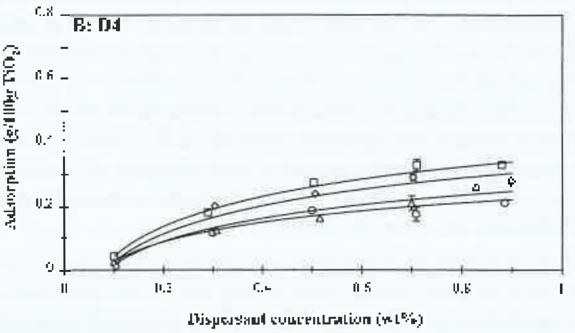


Figure 4B—Adsorption of α-olefin/maleic acid co-oligomer dispersants (D4/MA) on titanium dioxide pigments surface-treated with mixed inorganic oxides. Symbols: (□) sample 5, (◇) sample 6; (Δ) sample 4, and (○) sample 3.

the surface of TiO_2; whereas, in sample 5, the IEP indicates that Al_2O_3 is the primary surface component. In sample 6, although ZrO_2 is applied in an equal amount to Al_2O_3 (1 wt%), the IEP indicates that the surface is primarily Al_2O_3.

It might be expected that at a pH of 9.3, the higher IEP surfaces with remaining hydroxyl 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, [C_8H_{17}–(D8)/MA and C_4H_9 (D4)/MA] from a dispersion medium of pH 9.3 (*Figures* 4a and 4b) parallel the substrate IEP values of the treated TiO_2. The adsorption of the C_4H_9– co-oligomer is again less than the C_8H_{17}– co-oligomer, but the dependence on the metal oxide IEP is observed.

Surfactant Adsorption on Organic Dispersant and Metal Oxide-Treated TiO_2

The adsorptions of C_8H_{17}–$C_6H_4O(EO)_{10}H$, representative of the typical nonionic surfactant added to a pigment grind (*Figure* 5), on the α-olefin/MA oligomer dispersant/mixed oxide-treated TiO_2 surfaces generally follow the dispersant adsorption data (*Figures* 4a and 4b). This would be expected, since the nonionic surfactant does not adsorb[10,11] from alkaline solutions on the Al_2O_3 inorganic-treated TiO_2.

The amount of surfactant adsorbed was quantified by two techniques: SEC and UV absorbance of the aromatic surfactant in the aqueous phase; the adsorption studies were conducted in media of 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 a 7.5 value, paralleling an interior latex coating. When the smaller α-olefin/MA dispersant is used, there is a notable difference from the surfactant's adsorption on Al_2O_3-treated TiO_2 relative to the substrate with an excess of SiO_2 treatment. With the small pendant group (D4/MA), the α-olefin/MA dispersant adsorbs significantly less than the D8/MA dispersant; there is little to attract the nonionic surfactant to even the Al_2O_3/TiO_2 interface. But there is an exception with pigment 2, containing an excess of SiO_2. The amount of surfactant absorbed increases with SiO_2 treatment. The surfactant adsorption data (discussed later) are close to sample 1, which was treated with only Al_2O_3.

Competitive Adsorption of HEUR Thickeners

In these experiments, TiO_2 had been sequentially pretreated with Al_2O_3 (sample 1) or other mixed inorganic oxides (*Table* 3), then with an organic oligomeric dispersant, D4/MA or D8/MA, at a 0.3 g dispersant per 100 g of TiO_2 level, and finally with a nonionic surfactant, C_8H_{17}–$C_6H_4O(EO)_{10}H$, 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 diisocyanate, methylene bis- 4(3)-

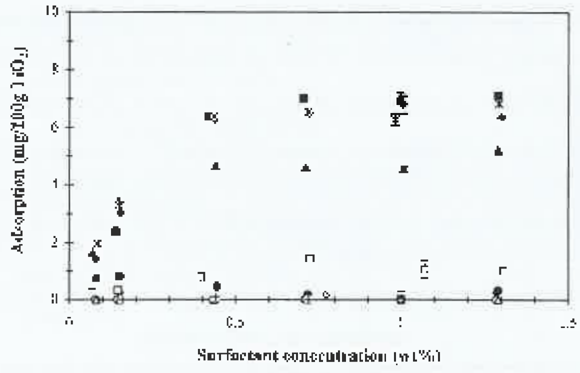


Figure 5—Adsorption (UV analysis) of nonionic surfactant C_8H_{17}–C_6H_4O–$(EO)_{10}H$ on TiO_2 pretreated with co-oligomeric dispersants and metal oxide. Symbols (Table 3): (□) sample 5, (◇) sample 6, (✱) sample 1, (Δ) sample 4, and (○) sample 3. Closed symbol: D8, open symbol: D4. Closed symbol: preadsorbed D8/MA; open symbols: preadsorbed D4/MA dispersant.

cyclohexyl diisocyanate ($H_{12}MDI$) units, at the EO terminal positions. A generalized structure for the model uniHEURs, 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 and residence time in hydrophobic associations increase with increasing terminal hydrophobe size, and the viscosity increases with increasing terminal hydrophobe size. Consistent with those studies, the larger terminal sizes in this HEUR series were more effective in displacing the formulation surfactant, C_8H_{17}–$C_6H_4O(EO)_{10}H$, from model poly(methyl methacrylate) latex surfaces.[6,15] Consistent with the need for a hydrophobic interaction, less HEUR is adsorbed on TiO_2 pretreated with the smaller MA/D4 than on the MA/D8 dispersant (*Figure* 6a). However, the dramatic adsorption differences noted among different terminal hydrophobe sizes in the latex studies are not evident in either the narrow molecular weight (*Figure* 6a) or Step-Growth (*Figure* 6b) HEURs in the TiO_2 adsorption studies. As expected, there is greater adsorption with the narrow molecular weight uniHEURs than with the S-G HEURs because of the relative purity of the former thickener.

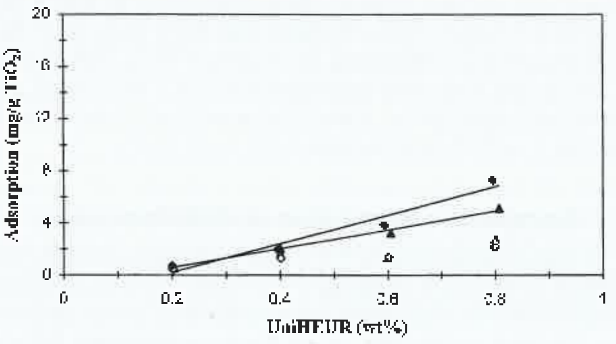


Figure 6a—Competitive adsorption on Al_2O_3-treated TiO_2 of uniHEUR thickener R–(H_{12}MDI–$(EO)_{530}$–H_{12}MDI)–R on sample 1 (Table 3) prestabilized by D4/MA (open symbol) or D8/MA (closed symbol) dispersant in the presence of 0.8 wt% nonionic surfactant C_8H_{17}–C_6H_4O–$(EO)_{10}H$. Symbols: (◊) R= $C_{13}H_{26}$, (Δ) R= C_8H_{17}.

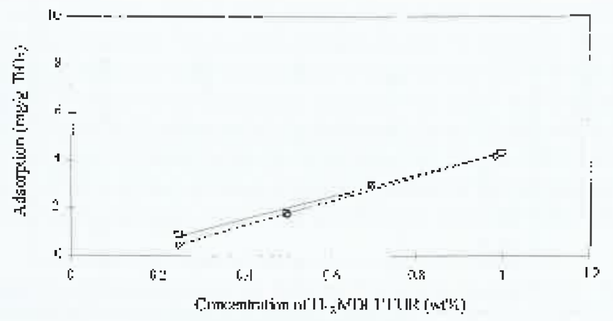


Figure 6b—Adsorption of different terminal alkyl chain length step-growth HEURs (R'–NH–CO–NH–C_6H_{10}–CH_2–C_6H_{10}–(NH–CO–O–$(CH_2CH_2O)_{198}$–CO–NH–C_6H_{10}–CH_2–C_6H_{10}–)$_3$–NH–CO–NH–R' HEUR association thickeners onto Al_2O_3/TiO_2 stabilized by D8/MA dispersant with 0.8 wt% level C_8H_{17}–$C_6H_4O(EtO)_{10}H$ nonionic surfactant presence. Symbols: (❑) R'=C_8H_{17}, (◊) R'=$C_{12}H_{25}$.

The effect of the metal oxide treatment of the TiO_2 surface on the ultimate adsorption of a $C_{12}H_{25}$–[H_{12}MDI-$(EO)_{530}$–H_{12}MDI]–$C_{12}H_{25}$ uniHEUR thickener follows the IEP of the pigment's surface when the organic dispersant D8/MA is adsorbed on the oxide surface. When TiO_2 is pretreated with D4/MA dispersant, the adsorption of uniHEURs on pigments is very low.

Surfactant Displacement

In a prior study,[17] a series of very large hydrophobe, model organic dispersants (the $C_{10}H_{20}$, $C_{14}H_{28}$, and $C_{18}H_{36}$ α-olefin co-oligomers with maleic acid, sodium salt) were adsorbed onto a Al_2O_3 pretreated TiO_2. The individual formulation surfactant, C_8H_{17}–$C_6H_4O(EO)_{11}H$, and two model associative thickeners of the uniHEUR type[8,10] were 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 oxyethylene 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 chemical structures.

The surfactant, C_8H_{17}–$C_6H_4O(EO)_{10}H$, 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 TiO_2 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[9] terminal hydrophobe of the HEURs, the more efficient it

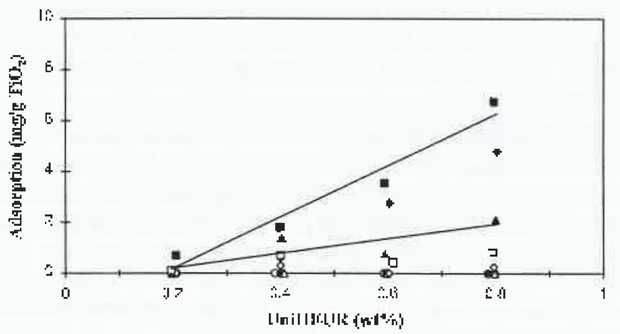


Figure 7—Competitive adsorption of uniHEUR thickener $C_{12}H_{25}$–(H_{12}MDI–$(EO)_{530}$–H_{12}MDI)–$C_{12}H_{25}$ on TiO_2 pigments (Table 3) prestabilized by D4/MA (open symbol) or D8/MA (closed symbol) dispersant in the presence of 0.8 wt% nonionic surfactant C_8H_{17}–C_6H_4O–$(EO)_{10}H$. Symbols: (❑) sample 5, (◊) sample 6, (Δ) sample 4, and (○) sample 3.

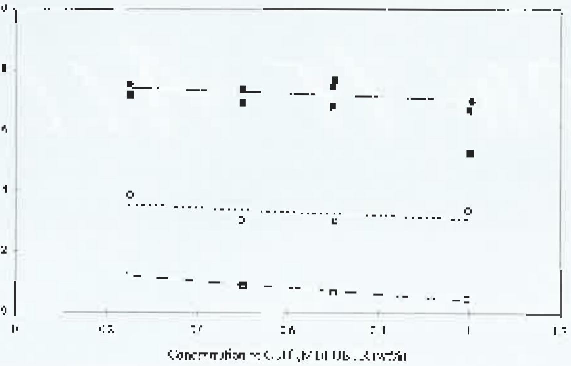


Figure 8 —Displacement of 0.8 wt% level C_8H_{17}–$C_6H_4O(EtO)_{10}H$ nonionic surfactant on Al_2O_3/TiO_2 (■, solid line, containing a very small amount of SiO_2) and SiO_2/TiO_2 (○, dotted line) by increasing the concentration of $C_{14}H_{29}$–NH–CO–NH–C_6H_{10}–CH_2–C_6H_{10}–[NH–CO–O–$(CH_2CH_2O)_{198}$–CO–NH–C_6H_{10}–CH_2–C_6H_{10}–$]_5$NH–CO–NH–$C_{14}H_{29}$ HEUR associative thickener by SEC. Closed symbol—pigment pretreated with D8/MA dispersant; open symbol—pigment pretreated by D4/MA dispersant. Solution pH = 7.5.

would be. In reality, when the H_{12}MDI–HEURs were adsorbed (SEC technique), the formulation nonionic surfactant (UV analysis of the free solution concentrations) did not desorb significantly from the metal oxide/TiO_2 surface (*Figures* 7 and 8) pretreated with the larger D8/MA dispersant; however, this is not observed when the smaller D4/MA is added to the metal oxide/TiO_2 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 Al_2O_3 pretreated TiO_2 dispersion; however, there is a significant amount of association in the presence of HEUR thickeners when the metal oxide treatment is SiO_2.

CONCLUSIONS

The metal oxide treatment of the TiO_2 surface influences the amount of dispersant adsorbed. In adsorption from pH 9.3 aqueous media, the amount of adsorption increases as the isoelectric point of the metal oxide-treated TiO_2 increases. It would be expected that at a pH of 9.3 the higher IEP surfaces would more readily participate in a hydrogen bonding or acid-base interaction with maleic acid co-oligomer dispersants that have high pK_as, and this would promote greater adsorption. The size of the co-oligomer pendant group also influences the amount of maleic acid co-oligomer adsorbed, and it is observed that adsorption of the C_4H_9– co-oligomer is lower and less sensitive in its adsorption to different inorganic oxide treatments of TiO_2 than a C_8H_{17}–/maleic acid co-oligomer. Within this matrix, when the metal oxide on the TiO_2 surface is Al_2O_3, the nonionic surfactant does not adsorb significantly on pigments pretreated with the smaller organic dispersant with pendant C_4H_9– units. The surfactant does adsorb on the smaller dispersant-treated TiO_2 when the metal oxide is primarily SiO_2 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 C_8H_{17}– dispersant on the Al_2O_3-treated TiO_2, the nonionic surfactant is not displaced by the adsorbing HEUR thickener.

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