Unifying Model for Understanding HEUR Associative Thickener Influences on Waterborne Coatings: I. HEUR Interactions with a Small Particle Latex

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The structural features of associative thickeners influence their viscosifying properties in neat and surfactant containing aqueous solutions and in architectural coating formulations. Our understanding of the phenomena based on model associative thickener of the Hydrophobically modified Ethoxylate URethane (HEUR) type are presented. These studies provide general concepts in aqueous solutions, but they do not provide a quantitative model for understanding the influence of associative thickeners in coating formulations. To provide a more quantitative description, the interactions of associative thickeners with the film forming latex are considered in this study. This requires a knowledge of the free surfactant concentration in the formulation that depends on the residual amount present in the latex and the amounts added with the pigment grind, colorant, etc. The competitive interaction of the surfactants and associative thickener types for the surface of both disperse phases is a key variable. These interactions with the latex will be discussed in this article in an effort to define an encompassing model for understanding how HEUR associative thickeners influence waterborne coatings.

INTRODUCTION

Associative thickeners are noted for their sensitivity to variations in formulations, and there are a variety of structurally undefined, commercial associative thickeners available for use in architectural and original equipment manufacturing (OEM) coating formulations. To date, studies have presented mechanisms of association that are unrealistic in a coating due to the high concentrations used in aqueous solution studies. The amounts of associative thickener used in a coating formulation are much lower. This study attempts to provide a more unified concept of the contribution of associative thickener in coatings by considering viscosity contributions from their self-association, the interaction of surfactants in the formulation with the thickener, and the interaction of the HEUR thickeners with the latex.

Our initial studies[1,2] were conducted with model Hydrophobically modified, Ethoxylated URethane (HEUR) polymers. This family of associative thickeners was chosen for it is the only family that allows well-defined models to be studied. They are prepared by the direct addition of a monoisocyanate, such as octadecylisocyanate to a polyether diol or by the reaction of a telechelic polyether diisocyanate with an alkyl amine or alcohol. The thickeners prepared by either of these procedures are referred to as uniHEURs. Our study also will include both uniHEURs and HEURs prepared by a step-growth (S-G HEUR) polymerization,[3] the type used commercially. The influence of the synthesis procedures on the solution properties of both types of thickeners are reviewed in chapter 10 of reference (4).

The concentrations used in these previous aqueous solution studies are well above those used in coating formulations, and in general, the amount of surfactant present in a coating formulation is not at a concentration that would promote an optimum viscosity maximum [chapter 17 in reference (4)]. In addition to any viscosity contribution, the HEUR associative thickeners also serve to increase the stability of the disperse phases (i.e., titanium dioxide (TiO_2) and the latex), and these disperse phases contribute to the dispersion's viscosity through their "increased" volume fraction.[5,6] The objectives of

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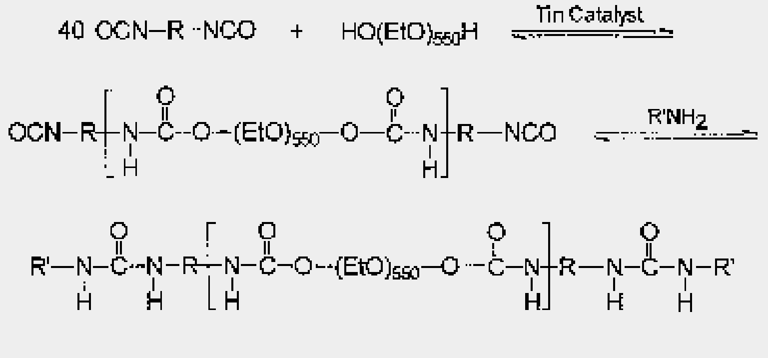
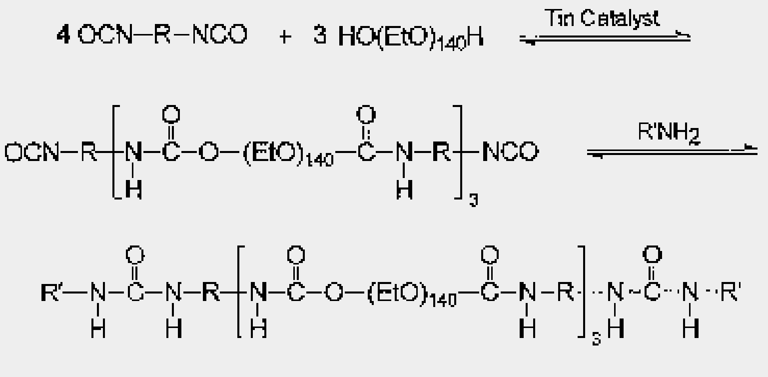


Scheme 1—Synthesis of narrow molecular weight distribution $C_{18}H_{37}$ "uniHEUR" thickeners.



Scheme 2—Synthesis of broad molecular weight distribution step-growth (S-G) HEUR thickeners.

the current study examine how the adsorption of the HEURs on the latex influences their rheology in the presence of surfactants. A key parameter in this study is the role of the free surfactant in the coating formulation.

EXPERIMENTAL

The materials used in these studies and procedures for measuring adsorption, individually and competitively, have been described previously.[5] Procedures used in rheological measurements and in formulating pigment grinds, latex dispersions, and coatings formulations also have been described.[1-3,7]

RESULTS AND DISCUSSIONS

In traditional cellulose ether thickened latex coatings, there is a competition for waters of hydration among the surfaces of TiO_2, the latex, and the thickener. In the depletion flocculation[8,9] concept the competition is compromised by liberation of water from and flocculation of the disperse phases, if they are not properly stabilized. Replacement of the cellulose ether thickeners with surfactant-modified, water-soluble polymers (W-SPs) provides a means for stabilization through adsorption of the thickener's hydrophobes on the disperse phases with displacement of or participation with the adsorbed, conventional surfactants. In addition to stabilizing the disperse phase, an association of the surfactant-modified W-SP with the disperse phases could influence dispersion rheology.

For significant adsorption to occur on the latex, the concentration of the conventional surfactants (arising from the residual amounts left from the latex synthesis and from that added to the pigment grind) should be relatively low. It also requires that the hydrophobes of the associative thickener be equivalent or larger in size than the hydrophobes of these conventional surfactants.

Adsorption on Small Particle Latexes

Both surfactants and HEUR thickeners will adsorb on a latex surface; it is a simple hydrophobic interaction between the surface of the latex and the hydrophobes of the surfactant or the thickener. It would be truly simple if the latexes were not complex. To achieve stability to salinity gradients in urban water supplies and to mechanical and thermal variations, latexes are synthesized with oligomeric acids or polymer fragments grafted to their surfaces.[10] These surface structures influence the amount of surfactant and associative thickener adsorbed. In addition, latexes, unlike TiO_2, are synthesized in various median particle sizes and particle size distributions, and latexes are often blended to obtain bi- and multimodal particle size distributions. For simplicity, our adsorption studies will be restricted to a small monodisperse, methyl methacrylate latex, with $1.418^{*} 10^{-3}$ meq/m^2 of methacrylic acid on the latex's surface, which in most of the studies to follow, was dialyzed free of the synthesis surfactant.

If a uniHEUR (*Scheme* 1) with large terminal hydrophobes is added to the model 121 nm, dialyzed latex, the adsorbed HEUR layer enlargement of the latex's effective volume fraction can be quantified. In this dialyzed latex, stabilized by the ionized oligomeric methacrylic acid segments, the influence of the uniHEUR on the viscosity with increasing latex volume fraction is evident (*Figure* 1), and Kreiger's dimensionless parameter approach[11] could be used to calculate the effective volume fraction increase due to the adsorption of the uniHEUR. This approach, however, would not really relate to the meaningful use of associative thickener in higher quality latex coating. The uniHEUR with $C_{18}H_{37}$– hydrophobes is very efficient in viscosifying latex coatings, and the formulations are very shear thinning (*Figure* 2). It is more appropriate to use a smaller hydrophobe S-G HEURs, synthesized by a slightly different approach (*Scheme* 2).

The general adsorption behavior of S-G HEURs on model MMA latexes with surface acids is illustrated in

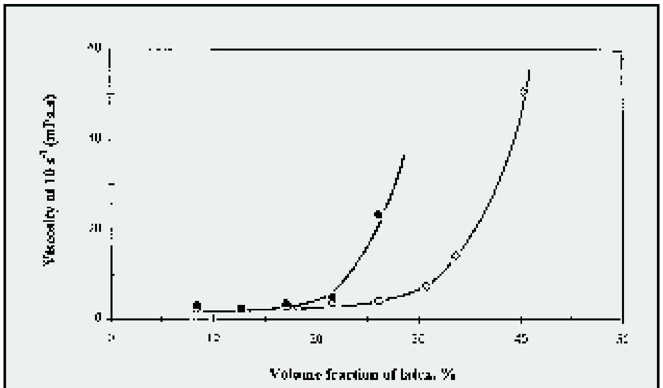


Figure 1—Viscosity build with increasing volume fraction of dialyzed 121 nm methacrylic acid/methyl methacrylate (P(MAA/MMA)) latex with 1.418 x 10^{-3} meq/m^2 surface acid. Symbols: (❍)—latex dispersion without thickeners; (●)—latex dispersion in the presence of model uniHEUR thickener $(C_{18}H_{37}NH-COO)_2(EtO)_{530}$ (0.025 g/g latex solid).

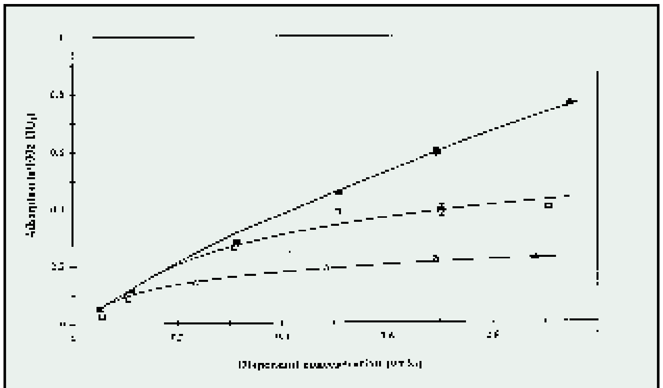


Figure 2—Shear viscosity profile of latex coating containing 0.07 volume fraction Al_2O_3/TiO_2 pigment, 121 nm acrylic latex with 1.418 x 10^{-3} meq/m^2 surface acid at 0.25 volume fraction, o-DIBMA dispersant, and 0.28 wt% model uniHEUR thickener $(C_{18}H_{37}NH-COO)_2(EtO)_{530}$. Open symbol—ascending shear rate curve; closed symbol—descending shear rate curve.

Figure 3. The adsorption of the thickeners containing small terminal hydrophobes follows a Langmuir adsorption isotherm (from a pH = 9.3 medium). As the terminal size of the S-G HEUR is increased, the adsorption behavior follows a more complex profile suggesting multilayer adsorption.

Commercial latexes are not dialyzed free of the synthesis surfactant, and in formulating a coating, nonionic surfactant is added with the pigment. Prior studies have shown that 1.0 wt% sodium dodecyl sulfate (SDS) will displace an S-G HEUR from the surface of a 140 nm acrylic latex[12]; however, SDS generally introduced with a colorant may not be the dominant surfactant in a coating formulation. An ethoxylated anionic surfactant (i.e., $C_9H_{19}–C_6H_4–O(EtO)_{20}SO_3NH_4$) is the surfactant we have used in synthesizing monodisperse methacrylate latexes. In the coating formulations that we have used, an ethoxylated, nonionic surfactant added to the pigment grind has been the dominant surfactant, and our emphasis has been on the competition of the terminal hydrophobes of the S-G HEURs and the hydrophobes of the nonionic surfactant for the latex surface. The chemical compositions of the surfactant and HEUR thickeners are very close; this makes quantification of the adsorbed species difficult. The aromatic unit in $C_8H_{17}–C_6H_4O(EtO)_{10}H$ permits quantification of the nonionic surfactant distribution in the aqueous phase; therefore, the dialyzed latex is titrated with the surfactant at a given thickener concentration. If the hydrophobes of the thickener are competitive with the surfactant, the adsorption density of the surfactant from the UV analysis will be less, and it is these types of studies reported in the following.

With increasing surfactant concentration, the HEUR thickener is displaced from the surface of the latex if there are no terminal hydrophobes (e.g., polyethylene glycol) or if they are small (*Figure* 4). This occurs at a relatively low surfactant concentration for HEURs with small terminal hydrophobes, but this displacement is only partial when the hydrophobe is large. In the latter case, the adsorption of the model uniHEURs on the latexes is noted to decrease the zeta potential of the latex. The stability of these dispersions is increased, despite the drop in electrical charge, due to the stability arising from the osmotic stabilization of the latex. This is a plus in media of increasing salinity. With these results in mind, we will turn to the rheology of such dispersions.

Rheology of Thickened Dispersions

The viscosity of a coating could be increased by increasing the volume fraction of the latex and TiO_2. With a soft, film-forming latex this would be courting disaster. Nevertheless, there is little question that the major viscosity contribution in a coating formulation

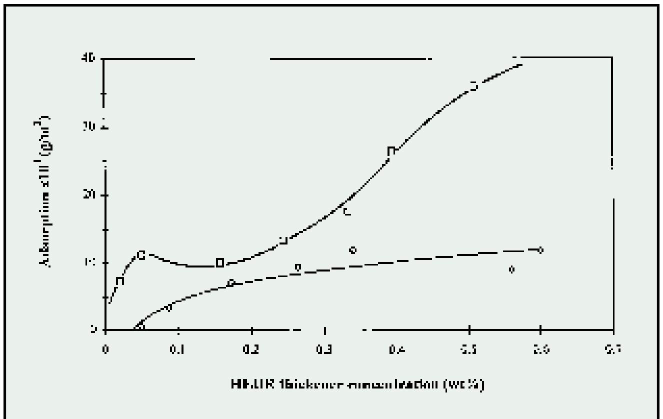


Figure 3—Adsorption isotherms of S-G HEUR thickeners on the 121 nm P(MAA/MMA) latex with 1.418 x 10^{-3} meq/m^2 surface acid at pH 9.3, determined by β-cyclodextrin complex method. Symbols (◊)—$C_6H_{13}–(H_{12}MDI–(EtO)_{180})_3–H_{12}MDI–C_6H_{13}$. (❑)—$C_{12}H_{25}–(H_{12}MDI–(EtO)_{180})_3–H_{12}MDI–C_{12}H_{25}$.

comes from the volume fraction contribution of the latex and TiO_2. The volume fraction one assumes when preparing a formulation is not the same as the actual volume fraction in the formulation due to the hydration of the disperse phases. For example, a latex formulation at the 0.32 volume fraction with a 5 nm hydration layer is effectively at a volume fraction of 0.42 for a 100 nm latex, and 0.36 for a 220 nm latex.[6] This is one of the reasons that small particle latexes require less water-soluble polymer as thickener to achieve a given KU viscosity. Even if an increase in the volume fraction achieved a given viscosity, without mass flocculation of the disperse components, it would not provide the viscosity profile necessary over the shear rate range approximating formulation, storage, and application. This is most economically done with a water-soluble polymer.

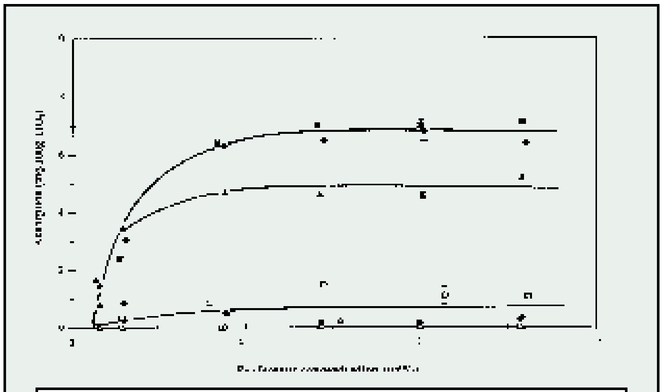


Figure 4—Adsorption density of C_8H_{17}–C_6H_4O–$(EtO)_{10}H$ on a 121 nm P(MAA/MMA) latex with 1.418×10^{-3} meq/m^2 surface acid in the presence of S-G and uniHEUR associative thickeners with $H_{12}MDI$ internal hydrophobes at pH 9.3 using a cyclodextrin complex method. (❍)—without thickener; (◊)—0.4 wt% C_6H_{13}–$(H_{12}MDI$-$(EtO)_{140})_3$–$H_{12}MDI$–C_6H_{13}; (❑)—0.4 wt% $C_{12}H_{25}$–$(H_{12}MDI$–$(EtO)_{140})_3$–$H_{12}MDI$–$C_{12}H_{25}$; (■)—0.4 wt% $(C_{18}H_{37}NH$–$COO)_2(EtO)_{180}$.

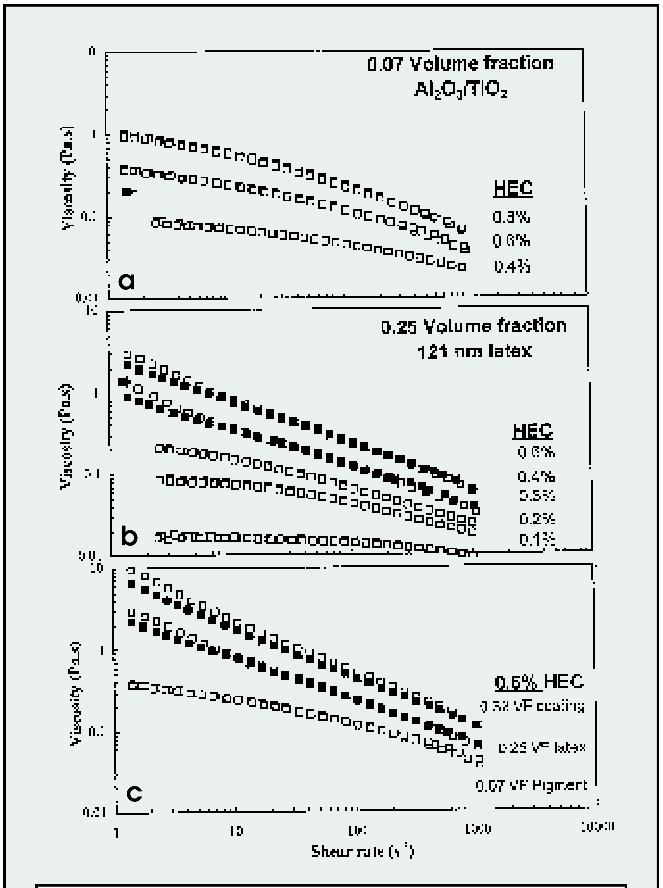


Figure 5—Shear viscosity profiles with different hydroxyethyl cellulose (HEC) concentrations:

(a)—In a pigment dispersion

(b)—Latex dispersion

(c)—Coating formulation.

Arrow indicates location of viscosity profile in 90 KU. Open symbol—ascending shear rate curve; closed symbol—descending shear rate curve.

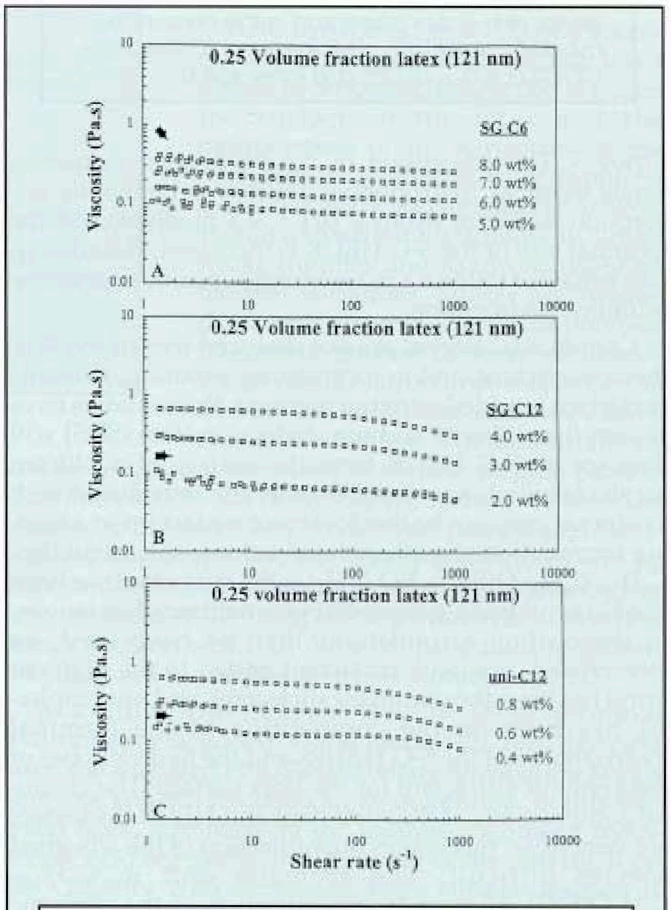


Figure 6—Shear viscosity profiles of 0.25 volume fraction 121 nm P(MAA/MMA) latex with 1.418×10^{-3} meq/m^2 surface acid (containing 0.86 wt% EP-115 $(C_9H_{19}$–C_6H_4–$O(EtO)_{20}SO_3NH_4)$) and 0.07 volume fraction pigment dispersion with model HEUR thickeners. Arrow indicates location of viscosity profile for 90 KU.

(a)—(C_6–SG HEUR): C_6H_{13}–$(H_{12}MDI$–$(EtO)_{140})_3$–$H_{12}MDI$–C_6H_{13}

(b)—(C_{12}–SG HEUR): $C_{12}H_{25}$–$(H_{12}MDI$–$(EtO)_{140})_3$–$H_{12}MDI$–$C_{12}H_{25}$

(c)—(C_{12}–uniHEUR): $C_{12}H_{25}$–$(H_{12}MDI$–$(EtO)_{550}$–$H_{12}MDI)$–$C_{12}H_{25}$

The viscosities of model HEURs, most commercial associative thickeners, and hydroxyethyl cellulose solutions are Newtonian or nearly so over a broad shear rate range at moderate concentrations. Slurries of TiO_2 or the latex, at the volume fractions used in coating formulations, are Newtonian in flow; however, when the thickeners and the disperse phases are blended together in a coating, the formulation can be markedly non-Newtonian. Our approach to understanding the complexities in a coating formulation is to examine the rheology of the disperse phases, individually and together, in the presence of the thickener, and in the presence of surfactants. The thickeners studied in the following discussion include HEC, two S-G HEURs, and a uniHEUR mentioned previously and in reference (4).

The pigment and latex volume fraction in a coating is generally 0.07 and 0.25, respectively. At this level with a 121 nm latex, the effective volume fraction of the latex is ca. 0.32, and significant shear viscosity increases, with thixotropy in the case of the latex, are observed at low shear rate viscosities at HEC concentrations below that required to thicken the formulation of 90 KU (*Figures* 5a-b). Clearly, depletion flocculation of the latex is the primary source of the extreme shear thinning in HEC thickened formulations. An excess of surfactant is required in the synthesis of a 121 nm latex, and it was not removed by dialysis in this initial study. The relative viscosity profiles of an HEC thickened 0.07 V.F. TiO_2 slurry, of an HEC thickened, 0.25 V.F. 121 nm latex, and of an HEC thickened architectural coating formulation containing 0.07 V.F. TiO_2 and 0.25 latex are illustrated in *Figure* 5c. Clearly, the individual viscosity of the coating is not a sum of the two thickened disperse phases. The higher viscosities at low shear rates are due to the additional "effective" increase in volume fraction, due to the inclusion of the aqueous phase in the depletion flocculated disperse phases in the higher solids (0.32 V.F.) formulation.

The three HEUR thickeners were also added to the latex, before dialysis, and all exhibited Newtonian flow, irrespective of the amount of HEUR used (*Figures* 6a-c). Significantly more of the $C_{12}H_{25}$–SG-HEUR is required (2.5 wt%) to thicken the formulation to a 90 KU than is required of the uniHEUR (0.5 wt%). This would be expected since the spectrum of products in a step-growth HEUR (i.e., ca. 20% of the polyethylene glycol PEG) remains unreacted and a significant amount is hydrophobe-modified, but unextended PEG are part of the synthetic mixture [chapters 10 and 17 in reference (4)]. Decreasing the terminal hydrophobe size to C_6H_{13}– in the SG-HEUR also decreases the thickening efficiency and 8.0 wt% of this thickener is required to formulate a 90 KU, 121 nm latex coating.

In the next series of studies, the synthesis surfactant was removed from the latex and incremental amounts of $C_{12}H_{25}SO_4Na$, C_9H_{19}–C_6H_4–$O(EtO)_{20}SO_3NH_4$ and C_8H_{17}–$C_6H_4O(EtO)_{10}H$ were added to simulate the type of surfactant that might be present in a coating as a result of addition of a colorant, the pigment grind or remaining from the synthesis of the latex. The concentrations of the surfactant added back to the dialyzed latex dispersion approximates the range that would be used in a latex coating. In the surfactant addition studies, the amount of thickener used approximates that added to achieve a formulation 90 KU viscosity. None of the three different surfactants influenced the rheology of the HEC thickened 121 nm latex (*Figure* 7) significantly, as was expected for the non-associating HEC thickener.

The HEURs also were added to the dialyzed 121 nm latex stabilized by the oligomeric surface acids. In the absence of surfactant, the HEUR thickeners will adsorb on the surface of the latex similar to the low volume solids data illustrated in *Figure* 3. With an increase in the effective volume solids, due to the adsorption, the viscosity of the dispersion will increase, as demonstrated in *Figure* 1. With the small hydrophobe SG-HEUR, the large amount of thickener required to obtain a 90 KU formulation viscosity, and weak hydrophobic association of the thickener would be expected to promote interparticle bridging.[13] This would explain the thixotropy in this formulation (*Figure* 8a) and higher viscosities at low

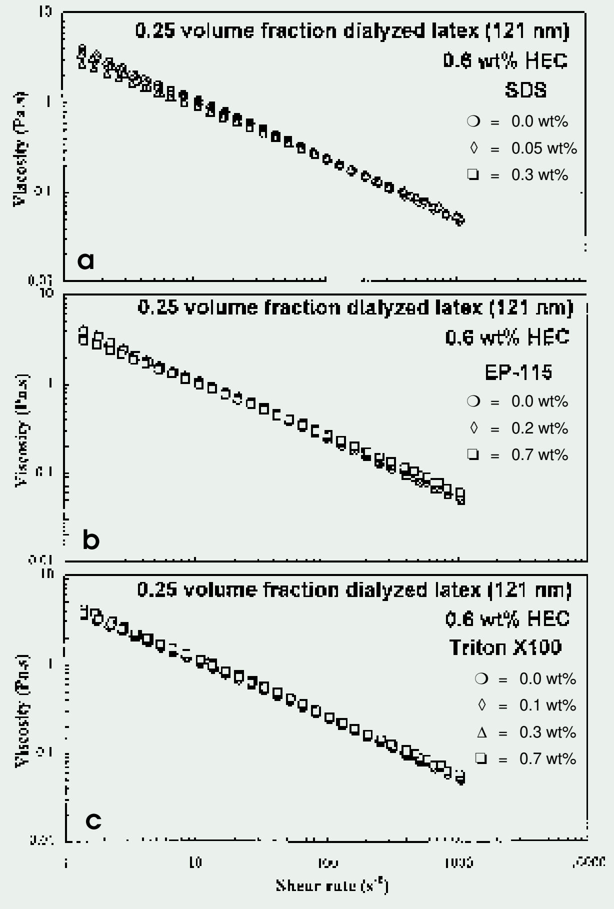


Figure 7—Shear viscosity profiles of 0.25 volume fraction 121 nm P(MAA/MAA) latex with 1.418 x 10^{-3} meq/m^2 surface acid 0.6 wt% HEC at different surfactant concentrations.
(a)—(SDS): $C_{12}H_{25}SO_4Na$
(b)—(EP-115): C_9H_{19}-C_6H_4-$O(EtO)_{20}SO_3NH_4$
(c)—(Triton X-100): C_8H_{17}-C_6H_4O-$(EtO)_{10}H$
Open symbol—ascending shear rate curve; closed symbol—descending shear rate curve.

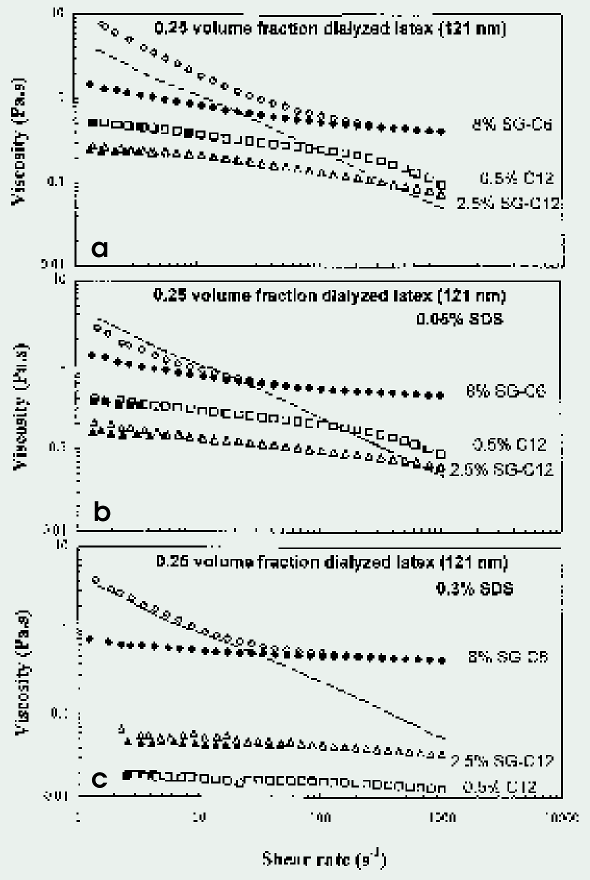


Figure 8—Shear viscosity profiles of 0.25 volume fraction 121 nm P(MAA/MMA) latex with 1.418 x 10^{-3} meq/m^2 surface acid with model HEUR thickeners at different SDS ($C_{12}H_{25}SO_4Na$) concentrations. The dashed line represents the corresponding HEC thickened latex. (C_6–S-G HEUR): C_6H_3–(H_{12}MDI–$(EtO)_{140})_3$–H_{12}MDI–C_6H_{13}; (C_{12}–S-G HEUR): $C_{12}H_{25}$–(H_{12}MDI–$(EtO)_{140})_3$–H_{12}MDI–$C_{12}H_{25}$; (C_{12}–uniHEUR): $C_{12}H_{25}$–(H_{12}MDI–$EtO)_{550}$–H_{12}MDI)–$C_{12}H_{25}$.

(a)—No SDS
(b)—0.05% SDS
(c)—0.3% SDS

shear rates than observed in the depletion flocculation (HEC thickened) dispersion; however, the addition of the hard surfactant, SDS, does not notably influence latex rheology (*Figures* 8b-c) with this high HEUR loading.

With SDS addition, the viscosities drop dramatically (*Figures* 8b-c) in the larger $C_{12}H_{25}$–HEURs thickened latex dispersions. In a previous study,[12] the addition of 0.5 wt% SDS resulted in complete displacement of a $C_{10}H_{21}$–HEUR from a similar size acrylic latex. In our latex, partially covered with methacrylic acid surface segments, the $C_{12}H_{25}$–HEURs also would be displaced completely from the surface of the latex. With the addition of 0.3 wt% SDS, the viscosity has fallen dramatically, except for the smaller hydrophobe HEUR thickened latex, at all shear rates. At this SDS concentration (slightly over one critical micelle concentration, CMC), there is no contribution to viscosity that is attributable to surfactant/HEUR interactions and all of the HEUR has been displaced from the surface of the latex. The viscosities (*Figure* 8c) are due to the volume fraction of the latex and the volume fraction of the thickener, determined in the absence of hydrophobic interactions, by the molecular weight and the amount of thickener added.

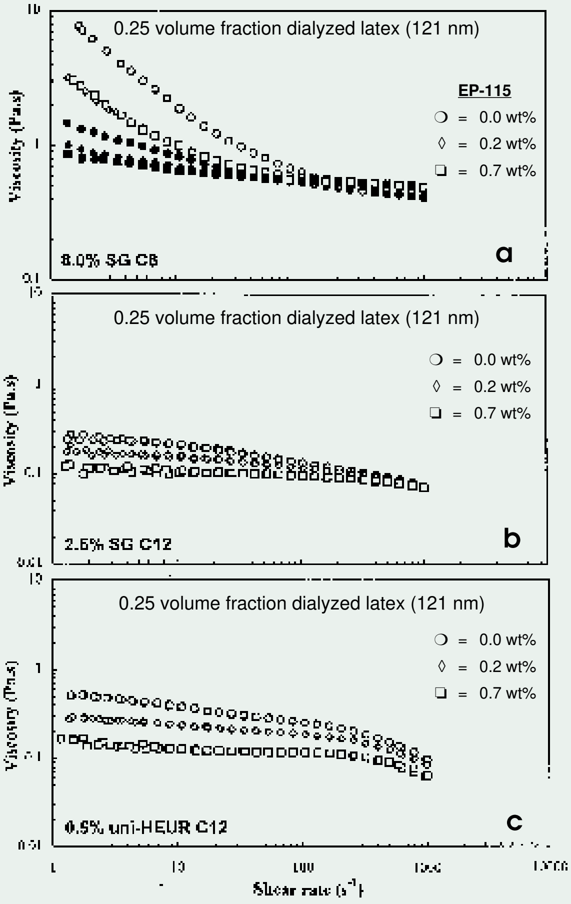


Figure 9—Shear viscosity profiles of 0.25 volume fraction 121 nm P(MAA/MMA) latex with 1.418 x 10^{-3} meq/m^2 surface acid with model HEUR thickeners at different EP-115 (C_9H_{19}–C_6H_4O–$(EtO)_{20}SO_3NH_4$) concentrations.

(a)—8.0% (C_6–SG HEUR): C_6H_{13}–(H_{12}MDI–$(EtO)_{140})_3$–H_{12}MDI–C_6H_{13}

(b)—2.5% (C_{12}–SG HEUR): $C_{12}H_{25}$–(H_{12}MDI–$(EtO)_{140})_3$–H_{12}MDI–$C_{12}H_{25}$

(c)—0.5% (C_{12}–uniHEUR): $C_{12}H_{25}$–(H_{12}MDI–$(EtO)_{550}$–H_{12}MDI)–$C_{12}H_{25}$

Open symbol—ascending shear rate curve; closed symbol—descending shear rate curve.

The surfactant present in the highest wt% in a coating is the nonionic surfactant added to the pigment grind. Adding this surfactant in greater amounts does not influence the rheology of the HEC thickened latex (*Figure* 7c), but the influence is notably different from SDS with the $C_{12}H_{25}$–HEURs. This is best illustrated by examining the surfactant concentration influences, collectively, with each individual HEUR thickener (*Figures* 9 and 10).

The surfactant, C_9H_{19}–C_6H_4–O(EtO)$_{20}$$SO_3NH_4$, added to the HEURs in *Figure* 9 is of intermediate hardness. With the smaller hydrophobe HEUR, the variations in rheology with surfactant addition are not dramatically different from those noted with SDS additions. With the larger $C_{12}H_{25}$–HEURs, the viscosity decreases are not as large at the higher surfactant concentrations, as were noted in the SDS additions. However, the addition of the nonionic surfactant, C_8H_{17}–C_6H_4O(EtO)$_{10}$H, to the dialyzed latex containing the small C_6H_{13}– terminal hydrophobe S-G HEUR (*Figure* 10a) dramatically decreases the viscosity at low shear rates and eliminates the dispersion's thioxotropy. At 0.7 wt% C_8H_{17}–C_6H_4O(EtO)$_{10}$H, the viscosity has dropped, not quite to the level reached with the addition of 0.3 wt% SDS, but unlike SDS, the thixotropy is absent with 0.7 wt% nonionic surfactant. The small C_6H_{13}–terminal hydrophobe S-G HEUR does not form strong associations. With the dialyzed latex stabilized with only the surface acid segments, adsorption of the C_6H_{13}–S-G HEUR will occur (*Figure* 3). The 8.0 wt% HEUR concentration used with surfactant addition is well above that legitimately used in adsorption studies, and multilayer adsorption could occur at 8.0 wt%. In any event the interactions with the latex surface are weak, as are hydrophobe interactions among the different HEUR chains. In the presence of even the nonionic surfactant the small hydrophobe HEUR is not adsorbed on the latex.

This is not true with the terminal $C_{12}H_{25}$– S-G HEUR and uniHEUR; they are not completely displaced from the latex surface with nonionic surfactant (*Figure* 4). The real distinction in these latex dispersions is the increase in viscosity with continued nonionic surfactant addition in both $C_{12}H_{25}$–HEUR thickened dispersions (*Figures* 10b-c). The nonionic surfactant does not displace all of the $C_{12}H_{25}$–HEURs from the latex surface, and the dispersions are not thixotropic. With SDS addition (*Figures* 8b-c), the viscosities decrease. The amount of C_8H_{17}–C_6H_4O(EtO)$_{10}$H used in our coating formulations is 0.65 wt%. This corresponds to 34 CMCs of surfactant relative to the 0.3 wt% SDS, that corresponds to 1.3 CMC. This high C_8H_{17}–C_6H_4O(EtO)$_{10}$H concentration, leading to higher viscosities, corresponds to the surfactant's micelle transformation from spheres to rods in the aqueous phase.

Based on the data in *Figures* 6 through 10, it is clear that the viscosities at higher shear rate (10^4 s^{-1}), important to hiding, are determined by the hydrodynamic volume contributions (related to the amount) of thickener, of a given MW, added to achieve a given KU formulation viscosity, just as it is in an HEC formulation.[14] In the C_6H_{13}–S-G HEUR thickened dispersion, this weakly associating HEUR is displaced (*Figure* 4 for data with C_8H_{17}–C_6H_4O(EtO)$_{10}$H) from the surface of the latex. This is reflected in *Figure* 8 at an intermediate shear rate of 20 s^{-1} in SDS solutions and at 200 s^{-1} in C_8H_{17}–C_6H_4O(EtO)$_{10}$H (*Figure* 10) solutions. With lesser amounts of the larger $C_{12}H_{25}$–HEURs, SDS is effective in displacing both the S-G and uniHEURs from the surface of the latex, and significant viscosity decreases are observed (*Figure* 8). Given the other surfactants present in a coating formulation and their possible synergies with SDS, hard surfactants should be avoided in HEUR thickened coatings. With increasing softness of the surfactant, the dramatic viscosity decreases are reversed with $C_{12}H_{25}$–HEURs. At levels typically used in the nonionic formulation surfactant, the viscosity of the dispersions increase, due to the participation of the HEURs in the rod-shaped nonionic surfactant micelles, and to the retention of a significant amount of these larger hydrophobe HEURs on the latex surface in the presence of nonionic surfactants (*Figure* 4).

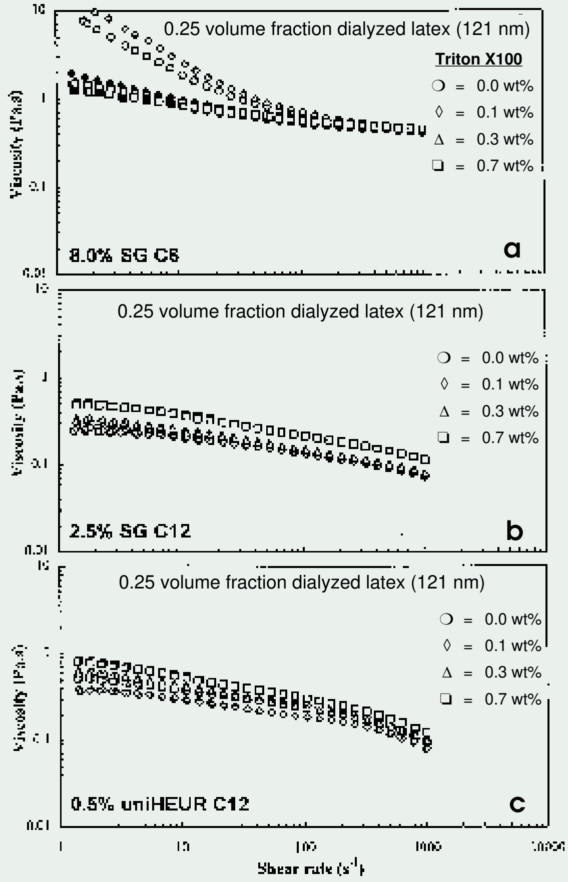


Figure 10—Shear viscosity profiles of 0.25 volume fraction 121 nm P(MAA/MMA) latex with 1.418 x 10^{-3} meq/m^2 surface acid with model HEUR thickeners at different Triton X-100 (C_8H_{17}–C_6H_4O–(EtO)$_{10}$H) concentrations.

(a)—8.0% (C_6–S-G HEUR): C_6H_{13}–(H_{12}MDI–(EtO)$_{140}$)$_3$–H_{12}MDI–C_6H_{13}

(b)—2.5% (C_{12}–S-G HEUR): $C_{12}H_{25}$–(H_{12}MDI–(EtO)$_{140}$)$_3$–H_{12}MDI–$C_{12}H_{25}$

(c)—0.5% (C_{12}–uniHEUR): $C_{12}H_{25}$–(H_{12}MDI–(EtO)$_{550}$–H_{12}MDI)–$C_{12}H_{25}$

Open symbol—ascending shear rate curve; closed symbol—descending shear rate curve.

CONCLUSIONS

To understand the influence of associative thickeners on the film properties and rheology of the formulation, our studies have centered on the adsorption of Hydrophobically modified, Ethoxylated URethane (HEUR) thickeners on the primary disperse phase components of a latex coating, the film forming binder, and the hiding pigment, TiO_2. The latter are discussed in Part II of this series. The data in this study are interpreted in terms of the interaction and displacement of HEURs from the latex surface by three types of surfactants found in a coating formulation, an anionic, an ethoxylated anionic, and a nonionic formulation surfactant.

It is clear that the viscosities at higher shear rate (10^4 s^{-1}), important to hiding, are determined by the hydrodynamic volume contributions (related to the amount of MW) of the thickener added to achieve a given KU formulation viscosity, just as it is in a HEC formulation. The examination of both Step-Growth HEUR and narrow molecular weight uniHEUR model thickeners revealed different sensitivities to the variety of surfactants in a latex coating. In the C_6H_{13}–S-G HEUR thickened dispersion, this weakly associating HEUR is displaced by the surfactants from the surface of the latex at an intermediate shear rate, 20 s^{-1} in SDS solutions; 200 s^{-1} in C_8H_{17}–$C_6H_4O(EtO)_{10}H$ solutions. With lesser amounts of the larger $C_{12}H_{25}$–HEURs required to thicken latex dispersions, SDS is effective in displacing both the S-G and uniHEURs from the surface of an acrylic latex, and significant viscosity decreases are observed. Given the other surfactants present in a coating formulation and its possible synergy with SDS, hard surfactants should be avoided in HEUR thickened coatings. With increasing softness of the surfactant (i.e., transition from anionic to nonionic), dramatic viscosity decreases are reversed. At levels typically used for the nonionic formulation surfactant in a coating, the viscosity of the dispersions increase, due to the participation of the $C_{12}H_{25}$–HEURs in rod-shaped nonionic micelles, and retention of a significant fraction of the $C_{12}H_{25}$–HEURs on the latex's surface.

HEUR associative thickener influences on the rheology of latex coatings are complex, but the mechanisms are understandable based on structural differences of the products and an understanding of basic surface chemistry principles.

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