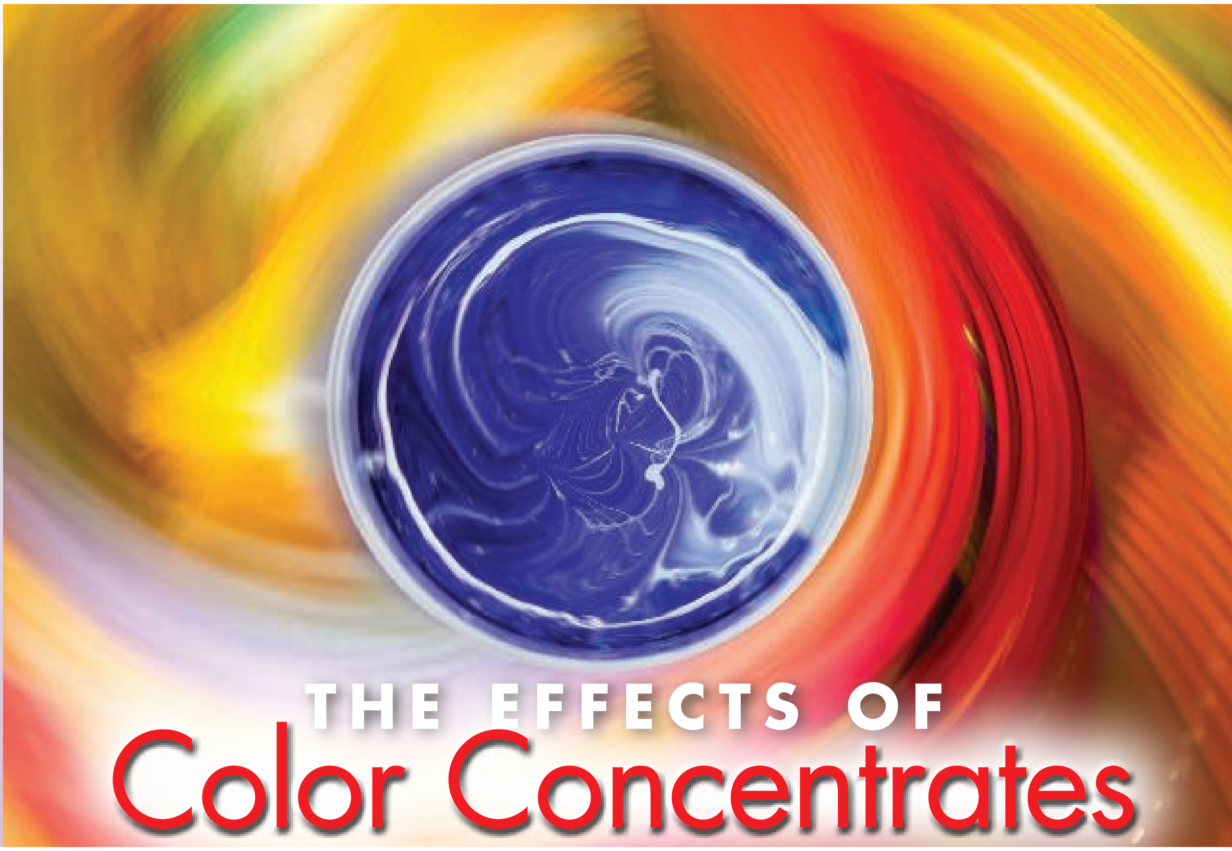

THE EFFECTS OF Color Concentrates on the Rheology of Tint Bases

By **Douglas J. Herrick**, **Jason W. Boke**, **Maung Y. Htet**, and **Raymond H. Fernando**
California Polytechnic State University

Rheological properties of coatings formulated with associative thickeners are quite sensitive to a number of formulation variables. Small changes in these variables, which include the latex, thickener, and surfactant components of the coating, can have a profound effect. Many previous studies have focused on understanding and controlling these sensitivities. However, few studies have focused on the relatively large viscosity drop and related problems when predispersed colorants are added to tint bases formulated with associative thickeners. In this study, pastel and deep-tone tint bases were formulated with associative and nonassociative thickeners. The tint bases were then tinted with six different conventional colorant dispersions and six low-VOC counterparts of the same colorants. Effects of the colorants, thickeners, and VOCs on viscosity profiles, dynamic viscoelastic properties, color development, and gloss were determined and results are presented.

Presented at the CoatingsTech Conference, sponsored by the American Coatings Association, March 11–13, 2013, in Rosemont, IL.

INTRODUCTION

The ability to control rheology is crucial in controlling the flow behavior of coatings during mixing and storage to application and flow out, leading to film formation. In general, viscosities in the range of several hundred mPa·s at application-related shear rates (10^3 s^{-1} and higher) are needed to achieve desired film thicknesses. Lower viscosities can cause the coating film to spread too thin. Preventing sagging of the applied films, on the other hand, requires viscosities in the range of 10–100 Pa·s at shear rates relevant to the sag-related flow (10^{-1} s^{-1} and lower). However, viscosities that are too high at low shear rates can prevent leveling flow that is required to achieve a uniform film. To meet these and other similar flow requirements, a typical waterborne coating must have a shear-thinning viscosity profile. Control of viscosity behavior and other rheological properties (yield stress, thixotropy, viscoelasticity, etc.) allow a formulator additional flexibility in designing the flow properties of the coating.

A typical, fully formulated coating without rheology modifiers is virtually Newtonian, with a viscosity of less than about 100 mPa·s. Therefore, addition of rheology modifiers to a coating formulation is essential in imparting the rheological properties discussed above. Until the late 1970s, several types of water-soluble polymers were commonly used as rheology modifiers for latex-based waterborne coatings. These polymers included cellulose derivatives (e.g., HEC-hydroxyethyl cellulose) and alkali-swellable acrylic emulsions.[1] Common issues associated with these thickeners include poor leveling (due to higher than desirable low-shear-rate viscosities), flocculation of dispersed particles, and water sensitivity of the dry films.

Introduction of associative thickeners in the late 1970s allowed formulators to control rheology while minimizing the problems outlined above. Associative thickeners are amphiphilic polymers containing both hydrophilic and hydrophobic groups in their structure, and can be ether non-ionic or anionic. Non-ionic associative thickeners available in the market today include hydrophobically modified, ethoxylated urethanes (HEUR), hydrophobically modified, aminoplast ethers (HEAT), and hydrophobically modified cellulose derivatives (e.g., HMHEC—hydrophobically modified, hydroxyethyl cellulose). Hydrophobically modified, alkai-swellable emulsions (HASE) represent a common example of an anionic associative thickener. The thickening mechanisms of associative thickeners are different and more complex compared to the mechanisms of the thickeners, such as cellulose derivatives that preceded them. Understanding these mechanisms in somewhat simplified systems (i.e., in aqueous media with few components, such as surfactants) has been the focus of numerous studies.[2,3] Several studies on fully formulated coatings have also been published.[2] These studies have clearly established that despite the many advantages associative thickeners offer, they are much more sensitive to formulation variables. These variables include the type of latex, surfactants, dispersants, and coalescing solvents.

One of the most difficult problems with the early-generation associative thickeners has been the high viscosity drop when predispersed colorants are added to tint bases at the point of sale.[4,5] This is due to the fact that predispersed colorants contain large amounts of surface active additives used to stabilize the finely dispersed colorant particles. Typical waterborne coatings are formulated to have viscosities in the neighborhood of 100 Krebs units of Stormer viscosity before colorant addition. Upon the addition of colorant, the viscosity of the coating can decrease by as much as 30–35 Krebs units.[4] In recent years, associative thickener suppliers have introduced a new generation of products to minimize the viscosity drop upon tinting. However, only a few reported studies[4,5] have focused on rheological analysis of this problem. The purpose of this study was to quantify the effects of colorant addition on the rheological properties, using commercially viable tint bases, colorants, and early generation associative thickeners.

Table 1—Pastel Base with HEC Thickeners

Ingredient	Solids (wt%)	Weight in Formulation (g)
Grind		
Water	0.00	50.00
Natrosol 250GR	4.00	50.00
Tamol 850	30.00	4.70
BYK-348	96.00	2.00
BYK-023	18.50	4.00
Nuosept 95	100.00	3.00
Minex-10	100.00	10.00
TiPure R902	100.00	230.00
Let-Down		
EPS-2757	50.00	448.00
Propylene Glycol	0.00	4.32
Texanol	0.00	8.96
BYK-023	18.50	8.00
Ammonium Hydroxide	0.00	1.00
Natrosol 250GR	4.00	126.00
Natrosol 250HR	2.00	143.70
Total Weight		1093.68
%Non-Volatiles by Weight (%NVW)		44.11
%Non-Volatiles by Volume (%NVV)		32.61
Pigment Volume Concentration (PVC)		21.77

Table 2—Pastel Base with HEUR Thickeners

Ingredient	Solids (wt%)	Weight in Formulation (g)
Grind		
Water	0.00	90.00
Acrysol RM-2020NPR	20.00	10.00
Tamol 850	30.00	4.50
BYK-348	96.00	2.00
BYK-023	18.50	4.00
Nuosept 95	100.00	3.00
Minex-10	100.00	10.00
TiPure R902	100.00	230.00
Let-Down		
EPS-2757	50.00	448.00
Water	0.00	227.50
Propylene Glycol	0.00	4.32
Texanol	0.00	8.96
BYK-023	18.50	8.00
Ammonium Hydroxide	0.00	1.00
Acrysol RM-2020NPR	20.00	11.50
Acrysol SCT-275	17.50	8.20
Total Weight		1070.98
%Non-Volatiles by Weight (%NVW)		44.65
%Non-Volatiles by Volume (%NVV)		32.08
Pigment Volume Concentration (PVC)		22.08

EXPERIMENTAL MATERIALS AND METHODS

Pastel Base Formulations

The pastel base formulations used in this study are shown in *Tables* 1 and 2. This is a formulation designed for use in high performance low- and zero-VOC paints. Both pastel bases were formulated to be as similar as possible, with the exception of the thickener. The formulation in *Table* 1 contained two hydroxyethyl cellulose (HEC) thickeners, one a low-molecular-weight

Table 3—Deep-tone Base with HEC Thickeners

Ingredient	Solids (wt%)	Weight in Formulation (g)
Grind		
Water	0.00	61.30
Natrosol 250GR	4.00	68.10
Tamol 850	30.00	0.70
BYK-348	96.00	2.91
BYK-023	18.50	8.30
Nuosept 95	100.00	4.10
Minex-10	100.00	13.60
Let-Down		
EPS-2757	50.00	611.00
Propylene Glycol	0.00	5.93
Texanol	0.00	15.70
BYK-023	18.50	8.10
Ammonium Hydroxide	0.00	1.50
Natrosol 250GR	4.00	102.70
Natrosol 250HR	2.00	139.80
Total Weight		1049.70
%Non-Volatiles by Weight (%NVW)		32.47
%Non-Volatiles by Volume (%NVV)		30.80
Pigment Volume Concentration (PVC)		1.73

Table 4—Deep-tone Base with HEUR Thickeners

Ingredient	Solids (wt%)	Weight in Formulation (g)
Grind		
Water	0.00	126.10
Acrysol RM-2020NPR	20.00	14.10
Tamol 850	30.00	0.70
BYK-348	96.00	2.94
BYK-023	18.50	9.30
Nuosept 95	100.00	4.30
Minex-10	100.00	14.10
Let-Down		
EPS-2757	50.00	628.30
Water	0.00	179.60
Propylene Glycol	0.00	6.11
Texanol	0.00	12.70
BYK-023	18.50	7.50
Ammonium Hydroxide	0.00	1.50
Acrysol RM-2020NPR	20.00	14.10
Acrysol SCT-275	17.50	17.90
Total Weight		1039.25
%Non-Volatiles by Weight (%NVW)		33.43
%Non-Volatiles by Volume (%NVV)		31.03
Pigment Volume Concentration (PVC)		1.75

(LMW) product (Natrosol 250GR) and the other a high-molecular-weight (HMW) product (Natrosol 250HR). The LMW HEC serves as the "high-shear-viscosity builder" and the HMW HEC serves as the "low-shear-viscosity builder." The formulation in *Table* 2 contains two non-ionic, HEUR associative thickeners (Acrysol RM-2020NPR as the high-shear-viscosity builder and Acrysol SCT-275 as the low-shear-viscosity builder). HEC thickeners were added in the form of aqueous solutions, prepared at least 24 hr prior to formulating the coatings, whereas the HEUR thickeners were added during mixing, as supplied. All ingredients in the grind were added in succession and dispersed to a Hegman fineness of grind rating of 7.5, followed by sequential addition of the let-down ingredients. After the formulation was completed, the Stormer viscosity was measured, and then measured again after 72 hr at rest. The solids fraction in each formulation was determined according to ASTM D2369.

Deep-tone Base Formulations

The deep-tone formulations used in this study were similar to the pastel bases described previously. The key difference is the removal of TiO_2 in each formulation (*Tables* 3 and 4).

Table 5—List of Colorants and Corresponding CI Pigments Used in This Study

Colorant (Low-VOC/Zero-VOC)	CI Pigment Name (Pigment)
1921/8821N Phthalo Green	PG7 (Phthalocyanine Green)
1982/8882N Magenta	PR122 (Quinacridone)
1977/8878N Yellow Oxide	PY42 (Yellow Iron Oxide)
1935/8835N Red Oxide	PR101 (Red Iron Oxide)
1913/8813N Yellow	PY74 (Monoarylide Yellow)
1991/8891N Lamp Black	PBK7 (Carbon Black)
1932/8832N Phthalo Blue	PB15:2 (Phthalocyanine Blue)

Colorant Addition

Two sets of seven colorants, supplied by EPS Color Corporation, were used for the study (*Table* 5). The CCA 1900 series represents conventional Universal colorants, and the 8800 series represents Zero-VOC colorants. The chemical compositions of the colorants are not available, but the main pigments used in each of the samples are included in *Table* 5. Forty grams of the premixed tint base were weighed into a plastic mixing cup, followed by addition of 5.0 g of colorant. The samples were mixed in a Thinky AR100 speed mixer for 60 sec, stirred vigorously with a spatula for an additional 20 sec, and then transferred to a 4-oz glass jar. The viscosity profile of each sample was obtained approximately 24 hr following colorant addition.

Table 6—Stormer Viscosities and Solids (% by Weight) in Tint Bases

Sample	% Solids by weight	LSV Thickener	HSV Thickener	Total Thickener	Initial Viscosity (KU)	72-Hr Viscosity (KU)
Pastel Base with HEC	44.22	0.26	0.64	0.90	85.0	86.7
Pastel Base with HEUR	44.84	0.13	0.40	0.53	95.4	98.7
Deep-tone Base with HEC	33.23	0.27	0.65	0.94	77.8	78.0
Deep-tone Base with HEUR	33.56	0.30	0.54	0.84	94.6	106.0

Rheology Characterization

The viscosity profile of each sample was obtained at 25°C with a TA Instruments AR2000 rheometer equipped with a 40 mm, 2° cone. The rheometer was run in a steady-state flow mode from 0.02–200 s^{-1} shear rate.

Each sample was stirred gently for about 15 sec with a spatula before analysis. HEC-containing samples were designated by the letter "N," the HEUR-thickened samples by the letter "A." For example, N-1921 would be the sample formulated with HEC and 1921 green colorant and A-8882N would be the sample formulated with HEUR and 8882N magenta colorant. Dynamic viscoelastic properties were determined under sinusoidal oscillatory conditions as a function of the shear strain (0.01–100% at 1 Hz frequency) and oscillatory frequency (0.1–100 Hz at 0.1% strain, unless indicated otherwise in the Results and Discussion section).

Gloss and Tint Strength Measurements

Immediately following the rheology analysis, drawdowns of each sample were prepared alongside their parent bases at a wet film thickness of 6 mils (1 mil = 0.001 in. = 25.4 microns). At least 24 hr of drying time were allowed for all drawdowns. Color measurements were made with a Datacolor Mercury spectrophotometer using a D65 standard illuminant. The contrast ratios were also determined from these measurements. Tint strengths were calculated according to the procedure outlined in ASTM D4838-88, using drawdowns of untinted bases as standards for each set of samples. Due to the lack of hiding power resulting from the absence of TiO_2, the only deep-tone base samples to achieve a contrast ratio sufficient to measure the tint strength (contrast ratios of 0.98 are required by ASTM D4838-88) were those with red oxide, yellow oxide, and black colorants.

RESULTS AND DISCUSSION

Viscosity Behavior of Tint Bases without Colorants

The solids content by weight and Stormer viscosities of all untinted formulations are shown in *Table* 6. The solids contents by weight are very close to the expected values in *Tables* 1–4. It should be noted that all of these coatings are formulated to have a nearly constant 32% solids by volume. The Stormer viscosities of HEUR-thickened bases are much closer to the target value of 100 KU; however, the HEC-thickened formulations' Stormer viscosities are significantly lower than the target value. Achieving high KU viscosities with HEC thickeners is always a challenge due to the fact that they were delivered to the formulation mix as very low-concentration aqueous solutions (2% and 4% by weight for HMW HEC and LMW HEC, respectively). These solutions are highly viscous, and increasing the HEC concentration in aqueous solution results in gels that are

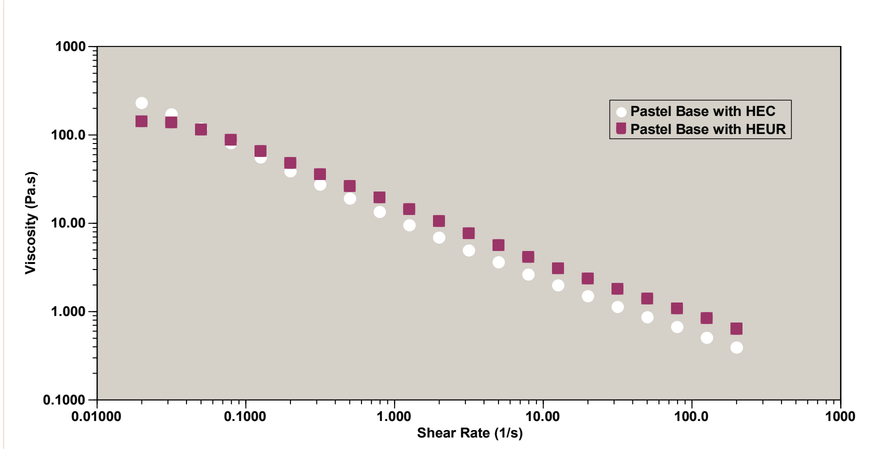

Figure 1—Viscosity dependence on shear rate of pastel bases with HEUR and HEC thickeners.

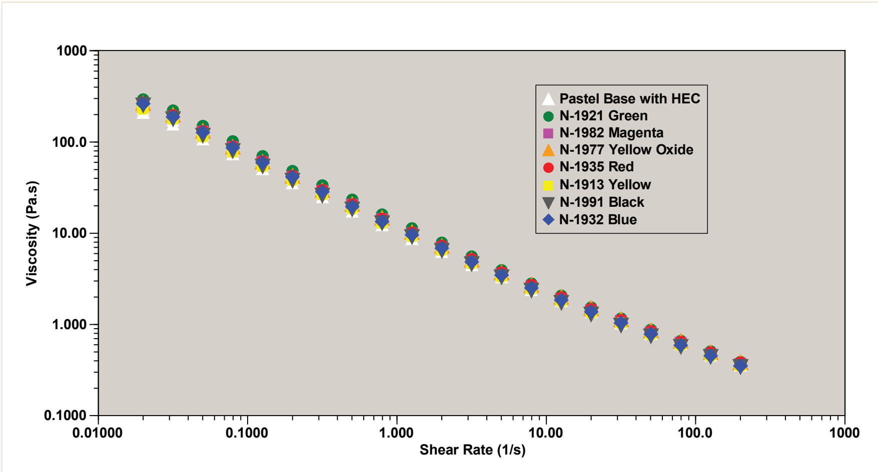

Figure 2—Effects of Universal colorants on viscosity behavior of HEC-thickened pastel bases.

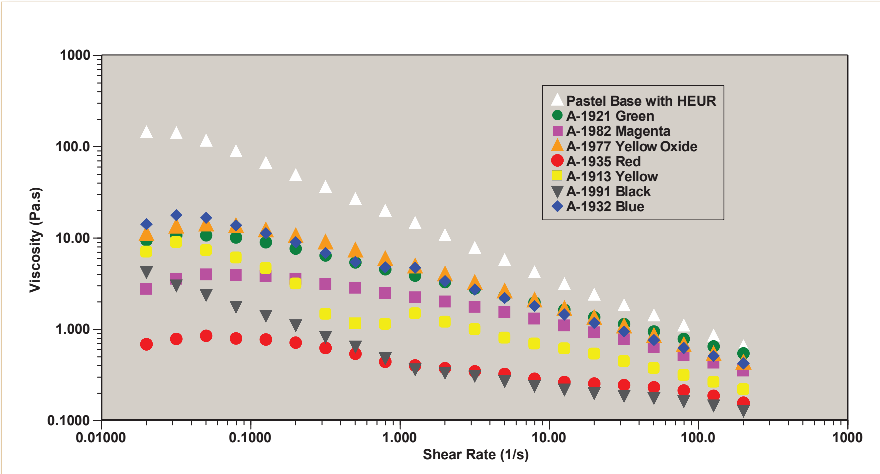

Figure 3—Effects of Universal colorants on viscosity behavior of HEUR-thickened pastel bases.

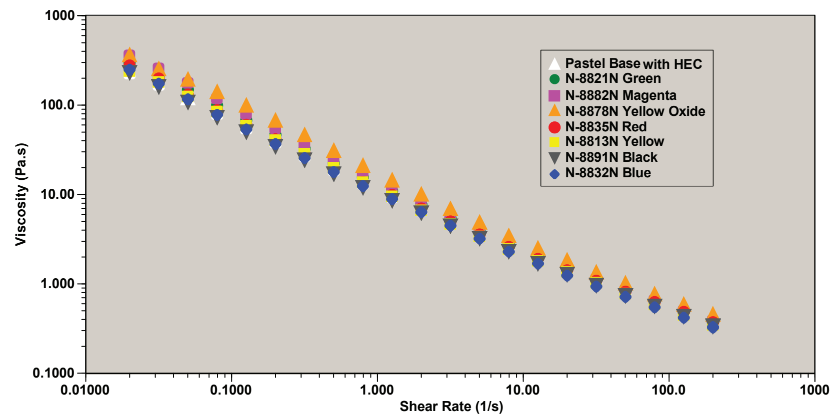

Figure 4—Effects of Zero-VOC colorants on viscosity behavior of HEC-thickened pastel bases.

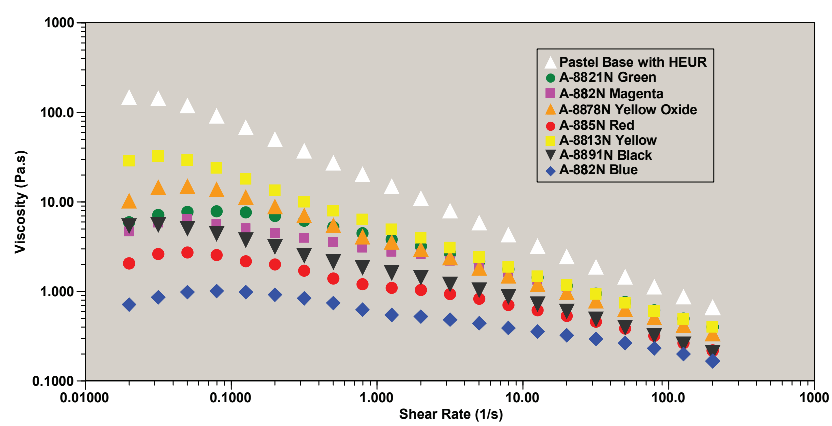

Figure 5—Effects of Zero-VOC colorants on viscosity behavior of HEUR-thickened pastel bases.

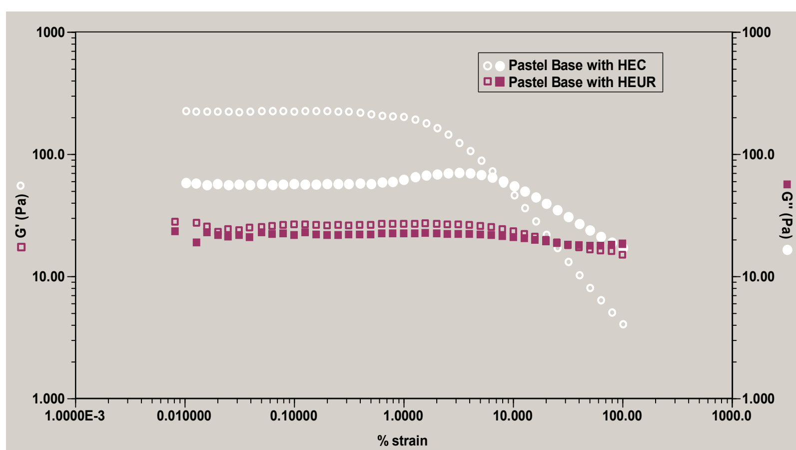

Figure 6—Dependence of storage and loss moduli (G' and G'') on % strain at 1 Hz frequency.

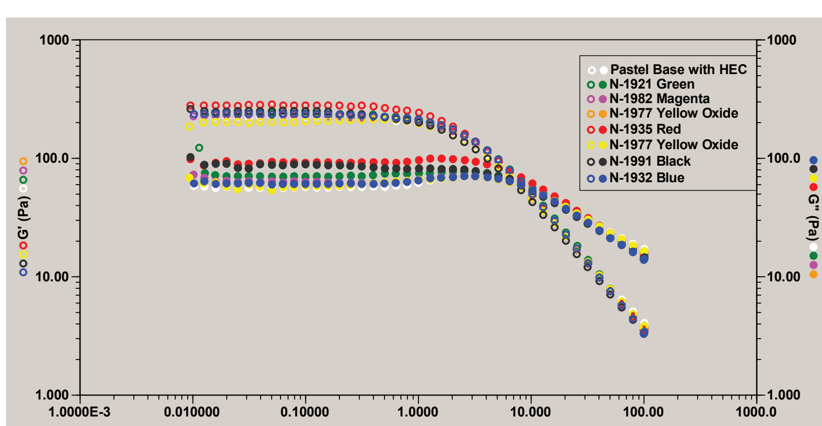

Figure 7—Dependence of storage and loss moduli (G' and G'') on % strain at 1 Hz frequency.

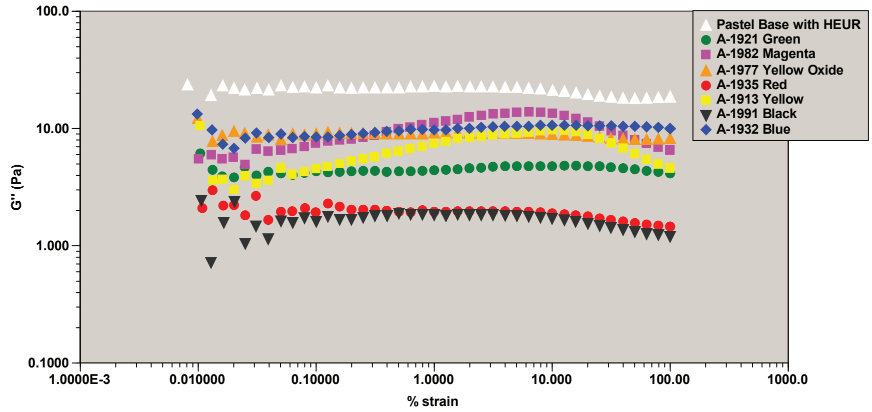

Figure 8—Dependence of loss modulus (G'') on % strain at 1 Hz frequency.

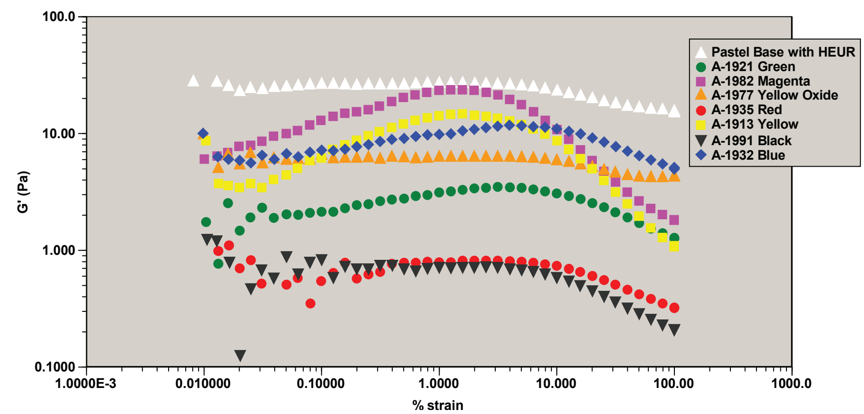

Figure 9—Dependence of storage modulus (G') on % strain at 1 Hz frequency.

difficult to incorporate. While industry practices may be adjusted (e.g., preparation of a highly concentrated aqueous slurry immediately before incorporation to the mix) to accommodate higher levels of incorporation to achieve a high KU viscosity, we chose to prepare solutions ahead of time to achieve complete solubilization of HEC. *Table* 6 includes the weight percentage of each of the two thickeners and the total thickener concentrations in the two pastel bases and the two deep-tone bases.

The viscosity dependence on shear rate for the two pastel bases thickened with HEUR and HEC thickeners is shown in *Figure* 1. Although the Stormer viscosity is low for the HEC-thickened base, its viscosity at the low-shear-rate end is higher than that of the HEUR-thickened base. Associative thickeners are more effective (at a lower total dosage) at increasing the viscosity at higher shear rates. This result is consistent with what has been reported in literature.

Effect of Colorants on Viscosity Behavior of Tint Bases

Viscosity profiles of pastel bases tinted with Universal colorants (1900 series) are shown in *Figure* 2 (HEC-thickened bases) and *Figure* 3 (HEUR-thickened bases). Viscosity profiles of untinted bases are also included for comparison. The virtual lack of sensitivity of the viscosity profile of the HEC-thickened formulation to colorants can be clearly seen in *Figure* 2. On the other hand, all colorants decrease the viscosities of HEUR-thickened base throughout the shear rate range of 0.02–200 s^{-1}. In addition, the viscosity profile of each of the tinted formulations is different. The highest viscosity drop is observed with the inorganic red oxide 1935. The viscosity profile of the sample containing 1913 yellow is erratic in the low-shear-rate region. This is often an indication of the presence of large aggregates of particles. Similar viscosity drop results were observed when the bases were tinted with Zero-VOC colorants (*Figures* 4 and 5). Viscosity drop caused by a given colorant between the Universal colorant series and Zero-VOC series is not consistent in several cases. For example, whereas the viscosity drop caused by 1932 blue (*Figure* 3) is modest, it is severe with 8832N blue (*Figure* 5). Results of deep-tone bases indicated similar trends.

Effect of Colorants on Dynamic Viscoelastic Properties of Tint Bases

Storage and loss moduli of the HEC- and HEUR-thickened pastel bases as a function of dynamic oscillatory strain (strain sweep experiment at 1 Hz frequency) are shown in *Figure* 6. The results are typical, with HEC-thickened formulations having high moduli at low % strains and decreasing at higher strains. The decrease in moduli is primarily due to disruption of intermolecular, interparticle, and particle-molecule interaction in the system. These interactions break up at higher strains to a point where the formulation's storage modulus is impacted more than its loss modulus. The HEUR-thickened formulation that shows evidence of a Newtonian plateau at low shear rates in *Figure* 1 exhibits near-linear viscoelastic behavior up to 100% strain.

Figures 7–9 show the effect of the 1900 series Universal colorants on the moduli of HEC- and HEUR-thickened pastel bases. Although there are significant differences in both G' and G'' values for the HEC-thickened tint base when tinted with different colorants (*Figure* 7), they are not close to the differences seen in *Figure* 8 (G') and *Figure* 9 (G'') for the HEUR-thickened tint base. Each colorant appears to disrupt the rheological mechanisms of the HEUR-thickened tint base differently.

Effect of Colorants on Other Properties of Tint Bases

The effects of colorants and thickeners on the gloss and tint strength were also determined. For untinted bases, HEUR-thickened films were higher in gloss than those thickened with HEC. This result is consistent with known effects of HEC and HEUR thickeners on gloss. HEUR-thickened formulations in this study have lower low-shear-rate viscosities that help leveling, and thus assist in improving gloss. HEC thickeners can lower gloss by flocculating the dispersed components as well. In general, tinting strengths of colorants were shown to be slightly higher with HEUR thickeners.

SUMMARY AND FUTURE WORK

The effects of Universal and Zero-VOC colorants on the rheology of HEC- and HEUR-thickened tint bases were examined. Viscosity profiles of HEC-thickened tint bases were virtually unaffected by the colorants. However, the viscosity of the HEUR-thickened formulation was lowered by all colorants. The level of effect was widely varied among colorants and between the two series of colorants. Current studies are focused on new generation commercial associative thickeners designed to minimize the viscosity drop upon addition of colorants. It is expected that the results of these studies will form the foundation for understanding complex interactions involved in effects of colorants on rheology of tinted formulations.

ACKNOWLEDGMENTS

Authors acknowledge the support provided by Dr. Pat Lutz (EPS Color Corporation), and financial support for Douglas Herrick provided by the Bill Moore Fellowship fund. CT

References

1. Schultz, D.N. and Glass, J.E. (Ed.), *Polymers as Rheology Modifiers,* ACS Symposium Series 462, American Chemical Society (1991).
2. Glass, J.E., "A Perspective on the History of and Current Research in Surfactant-Modified, Water-Soluble Polymers," *J. Coat. Technol.*, 73 (913) 79-98 (2001).
3. Fernando, R., Johnson, L., and Manion S., "Shear-Thickening in Aqueous Surfactant-Associative Thickener Mixtures," *J. Coat. Technol. Res.*, 8 (3*),* 299-309 (2011).
4. Saucy, D., "Avoiding Viscosity Loss on Tinting," *Paint & Coat. Ind.,* 34-38 (August 2008).
5. Mahli, D.M., Wegner, J.M., Glass, J E., and Phillips, D.G., "Waterborne Latex Coatings of Color: II. Surfactant Influences on Color Development and Viscosity," *J. Coat. Technol. Res.,* 2 (8), 635-647 (2005).

AUTHORS

Douglas J. Herrick, **Jason W. Boke**, **Maung Y. Htet**, and **Raymond H. Fernando**, Polymers and Coatings Program, Department of Chemistry and Biochemistry, California Polytechnic State University, San Luis Obispo, CA; rhfernan@calpoly.edu; www.polymerscoatings.calpoly.edu.