Next-Generation Rheology Modifier Technology

Novel Molecular Architecture for Breakthrough Sag/Flow Balance, Universal Viscosity Retention on Tinting, and Optimum Applied Hide

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In the architectural paint market, attention has focused on driving down volatile organic compounds (VOCs) while enhancing application performance for the do-it-yourself (DIY) market. This segment seeks products offering easy application, long-lasting performance, and excellent hiding, with a minimum number of coats. Ultimately, the desired goal is an applicator experience and performance result that can be differentiated in the market when evaluated by consumer market rating organizations. From a marketing perspective, how a paint feels when it is stirred, poured, and applied to the wall contributes to a unique end-user experience that helps to define the benefits of one brand over another. Rheology plays a key role in this area, directly affecting the in-can feel, as well as film thickness and finished smoothness of the final coating. An ideal rheology package is one that optimizes both sag resistance and flow across a range of shear. This is an ongoing formulator challenge due to the inherent characteristics of commonly used cellulosic thickeners and conventional hydrophobically modified ethylene oxide urethane (HEUR) rheology modifiers. Cellulosics offer excellent sag resistance, but they lack the properties needed to optimize flow. Conventional HEURs, by contrast, offer excellent flow, but often lack sufficient sag resistance. In typical paint formulations, optimizing one property means sacrificing the other to some degree. To address this performance conflict, a new category of HEUR thickeners has been developed that optimizes both sag resistance and flow, a combination heretofore unseen in commercial rheology modifiers.

This article describes the breakthrough molecular design of these next-generation HEURs, the unique balance of sag resistance and flow that results from this breakthrough design, and the added benefit of viscosity retention upon tinting which extends this sag/flow breakthrough

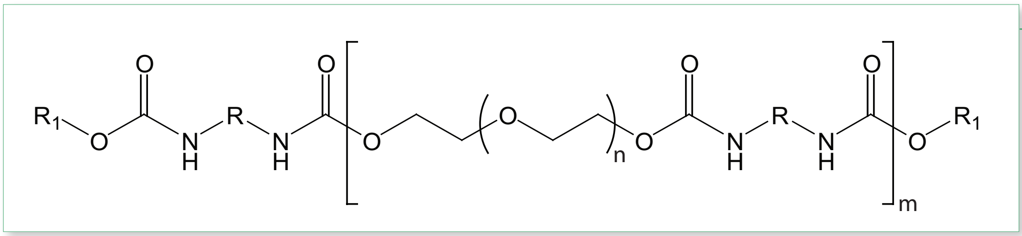

Figure 1—Generalized structure of HEUR rheology modifiers.

across the formulary spectrum. Additionally, this article will describe analytical and imagery tools developed to quantitatively characterize the pattern uniformity of roller-applied film, correlate these results with the impact on applied hiding in white and pastel paint formulations, and demonstrate significant improvements in applied hiding when both sag resistance and flow are optimized using next-generation HEUR technology.

CONVENTIONAL HEURS

HEUR rheology modifiers are widely used in waterborne coatings for their desirable rheological and application properties. They consist of a water-soluble polymer backbone that contains two or more hydrophobic groups. This general structure is shown in more detail in *Figure* 1.

Typical synthesis begins with preparing an isocyanate-terminated prepolymer by reacting polyethylene glycol (PEG) with excess diisocyanate in a ratio to achieve the target molecular weight (MW). Terminal hydrophobic groups are then introduced by end-capping this prepolymer with hydrophobic alcohols or amines. Pendant, or nonterminal, hydrophobic groups can also be introduced by including a hydrophobic diol in the prepolymer formation step. This process is depicted in *Figure* 2.

The hydrophobic groups of the HEUR polymer are unique in that they can associate with one another, as well as with other hydrophobic species and sites present in a coating formulation, especially the surface of latex binder particles. Such associations restrict molecular motion, thus increasing viscosity. The inherent thickening efficiency of traditional HEUR chemistry, however, can be problematic for the formulator from a handling standpoint. Associative rheology modifiers are designed to thicken aqueous systems very effectively, thus falling into two categories, with KU (Krebs Unit)-builders giving more viscous solutions than ICI-builders. Hence, most KU-builders become gels when dissolved at 20% solids in pure water, making them impractical to pump and pour. To avoid this problem, traditional HEUR technology dissolves the polymer in a mixture of water and solvent to achieve workable viscosities at reasonable polymer solids levels. The VOC contribution from such products limits their future use, as formulators strive to reduce or eliminate the VOC content of their coating systems.

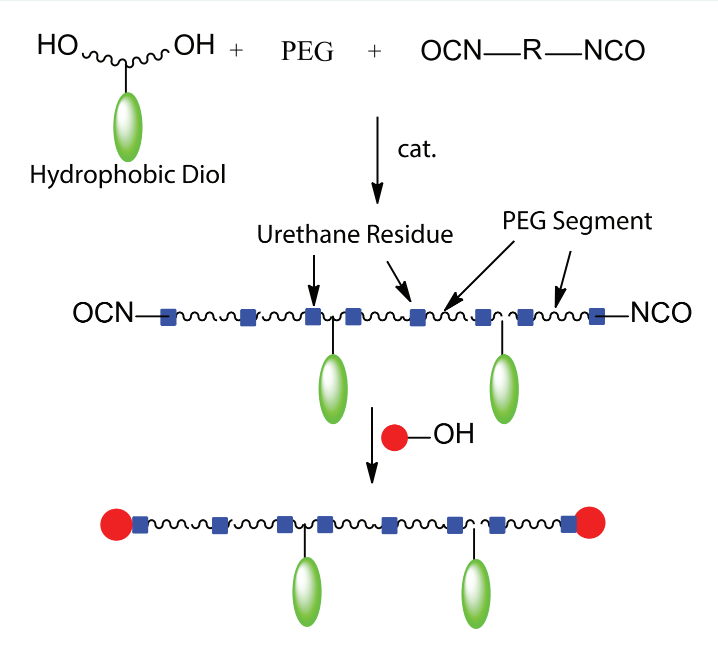

Figure 2—Synthesis of hybrid HEUR rheology modifiers with pendant and terminal hydrophobic groups.

pH CONTROL OF VISCOSITY

To facilitate the use of high-efficiency HEUR rheology modifiers in low-VOC and solvent-free paints, a novel technology has been developed that facilitates the delivery of HEUR technology at a level of as-supplied solids that is practical to pour and pump, without the aid of added solvent or surfactant. This technology, which is documented in U.S. Patent No. 7,741,402, is referred to as ACID SUPPRESSION™ HEUR Technology.[1] It is a pH-triggered approach where the associative thickening network can be turned on and off by a simple pH adjustment, thus facilitating delivery of the HEUR product in a solvent-free, aqueous solution at reasonable solids and viscosities.

The enabling feature of ACID SUPPRESSION HEUR Technology is the use of HEUR hydrophobic moieties that contain amine functionality. The presence of the amine nitrogen within the hydrophobe

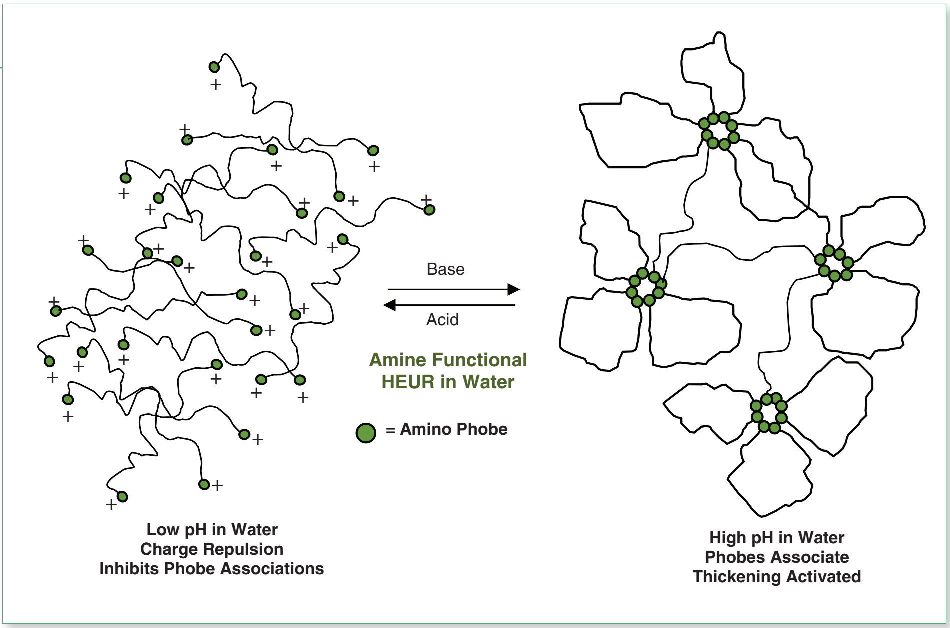

Figure 3—Schematic of the pH-triggered activation of associative thickening at high pH for HEUR polymers containing hydrophobic tertiary amine groups.

controls the ability to associate and form an associative network as a function of pH, as follows. At low pH, the amine is protonated and charged. The resulting charged hydrophobic groups of the HEUR thickener are less hydrophobic, which decreases the driving force to associate. The charged hydrophobic groups are inhibited from associating with one another in an aqueous solution due to charge-charge repulsion, further reducing the viscosity. In other words, thickening is turned "off" at a low pH. In the high-pH environment of an aqueous coating formulation, the amine is deprotonated and neutral, which results in full association and full thickening effect (i.e., at high pH, thickening is turned "on"). This approach is depicted schematically in *Figure* 3, where the charged nitrogen centers at low pH inhibit the association of the hydrophobic groups, while the neutral nitrogen centers at high pH exhibit full association.

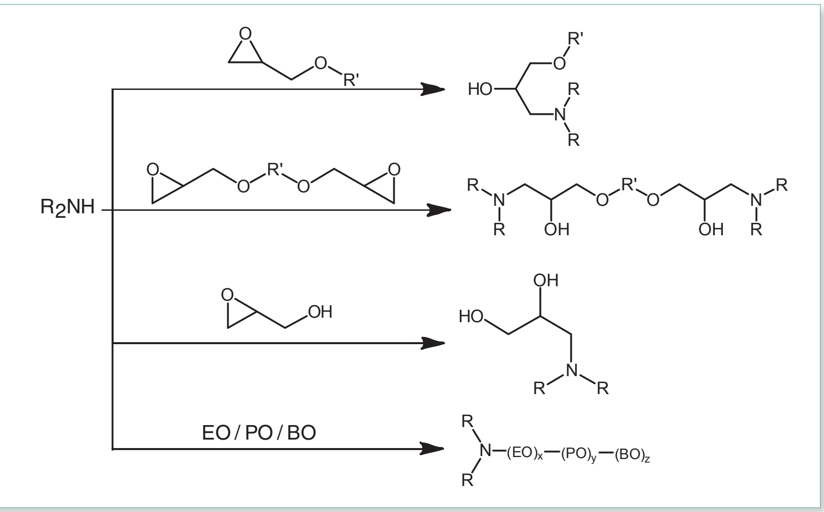

Figure 4—Epoxy-amine adduct chemistry: synthetic routes to hydrophobic amino alcohols.

AMINE HYDROPHOBES

A key challenge for developing products based on ACID SUPPRESSION™ HEUR Technology is the development of the necessary hydrophobic amines. Designing suitable hydrophobic amines to enable the new technology requires not only the right hydrophobicity, but also the right pKa, so that the thickener/nonthickener transition matches the formulation pH. The pKa is the pH at which half of the amine groups are ionized. Since the thickening mechanism of acid-suppressed HEURs is pH-triggered, the pKa of the hydrophobic amine must be such that the nitrogen is fully deprotonated in the pH environment of paint in order to achieve maximum thickening efficiency. Otherwise, small changes in the pH of the coating formulation could lead to significant viscosity changes.

A number of custom-designed hydrophobic amino alcohols and hydrophobic amino diols have been developed that are used to manufacture a variety of amine technology HEUR products. These key materials are produced through epoxy–amine chemistry, where appropriate alkyl and dialkyl amines are reacted with epoxides to form the corresponding amino alcohol adducts (*Figure* 4).[2-4] Examples of starting amines include diamylamine, dihexylamine, bis(2-ethylhexyl)amine, dibenzylamine, benzylamine, etc. Examples of epoxides include ethylene oxide, propylene oxide, butylene oxide, alpha-olefin epoxides, and various glycidyl ethers such as butyl glycidyl ether and 2-ethylhexyl glycidyl ether.

The effect of pKa on thickening response is displayed in *Figure* 5, where the viscosity of low-solids (2–4 wt%) aqueous solutions of HEUR rheology modifiers are shown as a function of pH. The set of HEUR rheology modifiers was synthesized using hydrophobic amino alcohols prepared as previously described, reacted with PEG8000 and isophorone diisocyanate.

For HEURs prepared using dialkylamine-based amino alcohols, such as bis(2-ethylhexyl)aminoethanol, the transition from low aqueous viscosity to high aqueous viscosity occurs over the pH range of approximately 6.0 to 8.5—thus, the pKa is ~7.4 for HEUR #1. For this particular HEUR to exhibit its maximum thickening efficiency, the pH of the formulation must be at 8.5 or above. For coating formulations where maximum thickening efficiency is required at lower pH, lower pKa hydrophobic amino alcohols, such as those based on benzylamine or dibenzylamine, were used to synthesize HEUR rheology modifiers with transitions from low viscosity to high viscosity that occur at a much lower pH. As seen in *Figure* 5, HEUR compositions can be tailored such that full thickening power is achieved at a range of pH values to suit the needs of specific coating formulations. For example, whereas the dialkylamine-based HEUR thickeners require pH above 8.5 to be fully activated, a benzylamine-based HEUR can be fully activated at a pH as low as 6.

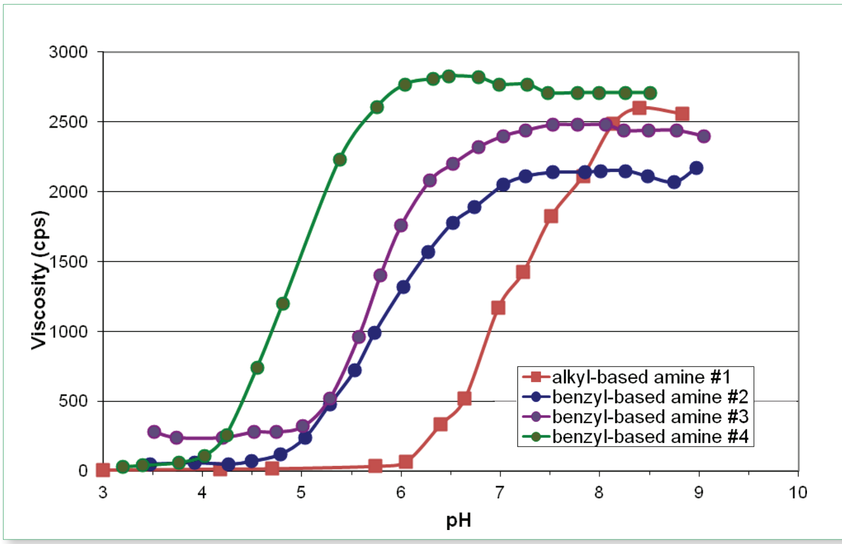

Figure 5—Aqueous solution viscosity vs pH for various rheology modifiers that vary in pKa based on ACID SUPPRESSION HEUR Technology.

ADDRESSING THE SAG/FLOW CONUNDRUM

Numerous factors, including hydrophobe size and structure, HEUR molecular weight, hydrophobe level, latex particle size and composition, and other coating formulation components, all contribute to the overall rheology profile of a given coating system and how the viscosity responds as a function of shear rate. As represented in *Figure* 6, addressing the full range of rheological needs for a typical paint requires a rheology package that delivers the necessary viscosity across a range of shear regions. In practice, this ultimately comes down to focusing on the low and high viscosity regimes. Conventional HEUR rheology modifiers generally fall into two classes: KU-builders are designed to thicken paints efficiently in the mid-shear range (approximately 100 sec^{-1}), whereas ICI-builders are designed to increase the viscosity at high shear rates (approximately 10,000 sec^{-1}) without giving a large increase in the mid-shear viscosity. Cellulosic rheology modifiers are often used as a third thickener to affect the low-shear (less than 10 sec^{-1}) regimes that conventional HEUR thickeners do not strongly influence.

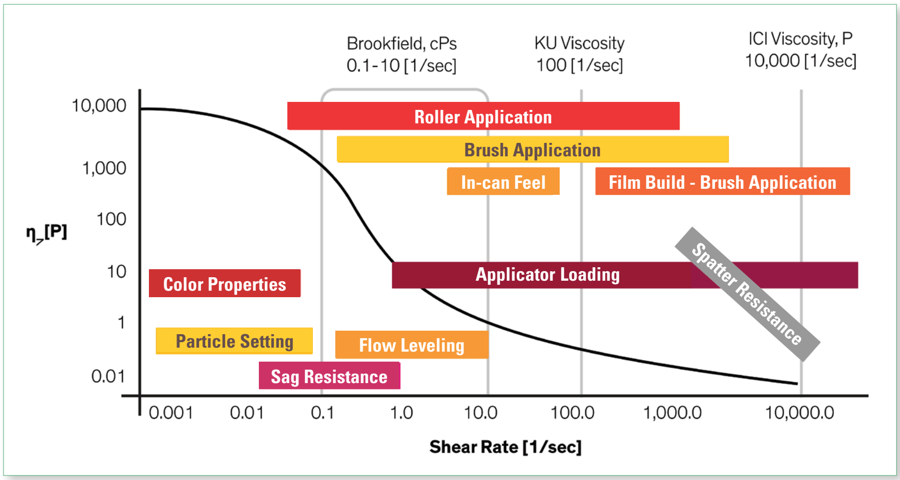

Figure 6—Rheology profile of a typical paint indicating the shear regions which correlate to various properties.

Finetuning the overall property balance of a paint formulation typically requires the use of a KU-builder, an ICI-builder, and a Brookfield-builder such as hydrophobically modified hydroxyethyl cellulose (HMHEC). Combinations help to facilitate an overall balance of rheological properties, including flow and leveling, sag resistance, syneresis resistance, film coverage, and roller/brush application properties; however, compromises in sag resistance and leveling are usually made to strike an acceptable balance of overall properties. As noted, an ongoing challenge lies in the optimization of sag resistance without sacrificing flow, and vice versa. As demonstrated by the green data points in *Figure* 7, Brookfield viscosity is highly correlated with leveling and sag resistance, but in opposite direc-

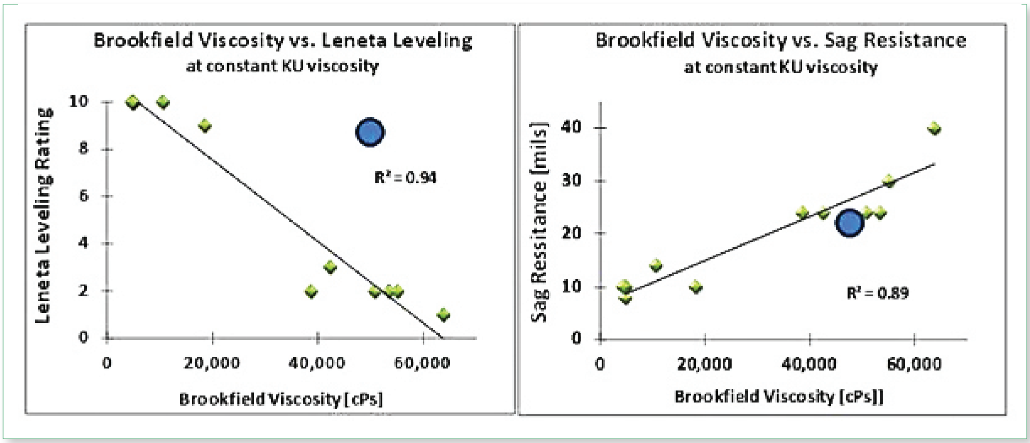

Figure 7—Low shear viscosity, as measured by a Brookfield-type viscometer, correlates well with both Leneta leveling and sag resistance. The blue circles represent high-performance HEUR rheology modifiers.

tions. As the Brookfield viscosity increases, the leveling of the paint film decreases, while the desired sag resistance increases. As a result, tipping the scale in favor of one property typically reduces the performance of the other.

Using ACID SUPPRESSION™ HEUR Technology as an enabling platform for low-VOC- and ultra-low-VOC-capable HEURs, new high-performance HEUR rheology modifiers have been designed to tip the scales in favor of both sag resistance and flow. These next-generation HEURS utilize newly designed hydrophobic amines (discussed above) to impart a novel combination of rheological properties, including a level of sag resistance that approaches the performance of cellulosics and a level of flow that is characteristic of conventional HEURs.

This breakthrough in sag/flow balance is demonstrated in *Figure* 8, which plots the rheology profiles of three paints thickened to the same KU and ICI viscosity. Paints formulated with HMHEC rheology modifier have the highest low-shear viscosity, and should, therefore, also have the highest sag resistance of the three paints. However, as shown in *Table* 1, the measured Leneta leveling and sag resistance of the high-performance HEUR rheology modifiers match the sag resistance of the HMHEC plus conventional HEUR co-thickened paint, but with the desirable additional benefit of significantly improved Leneta leveling. This breakthrough level of sag/flow optimization is represented by the blue data points in *Figure* 7, which demonstrate a performance balance previously unseen in rheology modifiers.

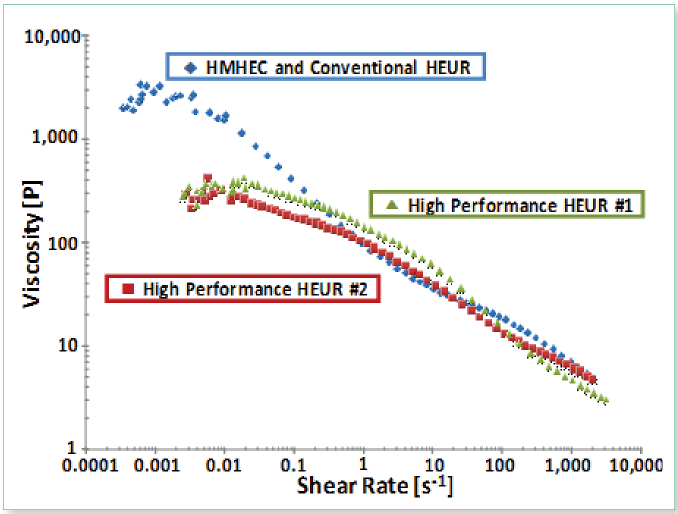

Figure 8—The effect of three thickener chemistries on rheological profile. All were adjusted to the same KU and ICI viscosity. These are for the same paints as in *Table* 3.

IMPACT ON APPLIED HIDING

In addition to providing a signature application experience, rheology plays a key role in the performance of the dried paint film. If the wet paint film does not flow and level once applied, it results in more peaks and valleys or thin and thick spots that are visible once the film is dry, which gives the appearance of a rough surface and poor pattern uniformity. However, the more

Table 1—Effect of Three Thickener Chemistries on Rheological Properties[a]

Semigloss Paint 30PVC/38VS	**HMHEC plus Conventional HEUR**	**High Performance HEUR #1**	**High Performance HEUR #2**
HMHEC	1.5 lb/100 gal	No	No
Equil. KU	111	105	110
Equil. ICI	1.6	1.6	1.5
Sag Resistance [mils]	24	22	24
Leneta Flow	3	9+	9

(a) All were adjusted to the same KU and ICI viscosity. These are for the same paints as in *Figure* 8.

Figure 9—Commercial paints qualitively and quantitively rated for surface smoothness. From left: Excellent (5), Very Good (4), Very Good (4), Good (3), Fair (2).

the paint sags and drips when applied, the less desirable it is to the customer and the more difficult it is to apply. As noted, conventional formulation practice uses cellulosic and HEUR rheology modifiers in combination to achieve a balance of sag resistance and flow. Dow scientists hypothesized that this widely accepted practice, which results in compromised leveling, negatively affects the pattern uniformity and, ultimately, the applied hiding of the coating. To prove this hypothesis and to demonstrate the impact of breakthrough sag/flow balance on applied hiding, Dow scientists developed a method of measurement to quantitatively rate film surface smoothness and correlate these findings with their impact on applied hiding.

Surface smoothness, surface roughness, and pattern uniformity are terms used to describe the texture or topography of a dried film when applied to a substrate, usually with a nap roller. Smoothness is typically rated visually on a scale of one to five, with one being poor or very rough and five being excellent, smooth, or uniform, as demonstrated in *Figure* 9. An ongoing concern with qualitative ratings based on visual observation is the variability from different operators over time.

To facilitate a deeper understanding of the influence of surface smoothness uniformity on applied hiding, Dow developed an analytical method that correlates visual imagery with measures for film topography. The method rates film roughness by comparing the surface area difference between the highest and lowest point of the paint film, a value calculated from the surface profile. The results are given as a difference in surface area between the imaged surface and a flat surface of the same lateral size. A data set was evaluated by visual rating, as well as surface area roughness, to understand the correlation between the two methods, and as a means to determine if visual appearance is related to the topography of dried films. *Figure* 10 shows the correlation between the visual rating by a 1–5 scale, and the surface area difference. The results show a good correlation between the image ratings and topography results, thus providing quantitative values that remove operator error. Topography maps also can be used to determine film thickness. The measured thick-

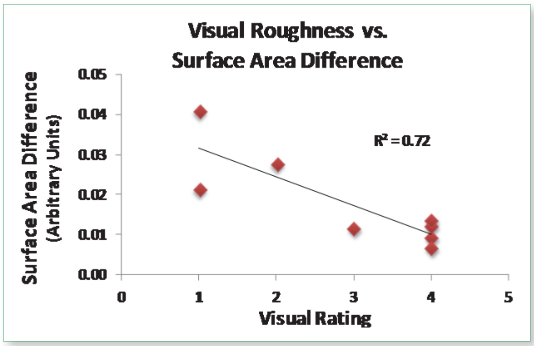

Figure 10—Visual surface roughness evaluation correlates well with the more time-consuming topography measurement.

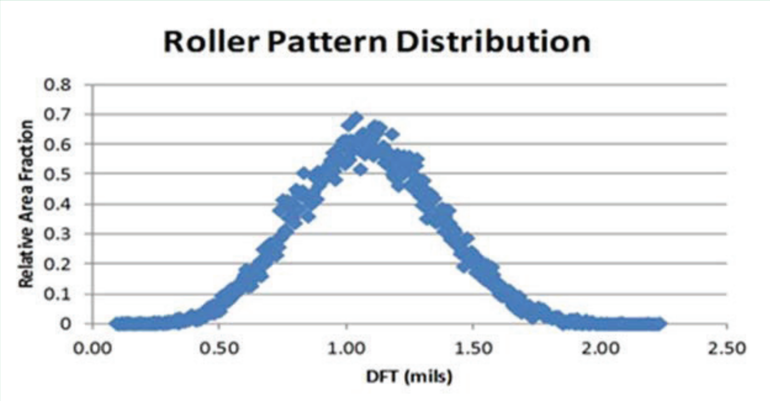

Figure 11—Roller patterns are described based on the Relative Surface Area of each measured dry film thickness (DFT). These patterns can be approximated by Gaussian distributions. For the pattern shown, the average is 1.05 mil and the standard deviation is 0.24 mil.

Table 2—Estimated Contrast Ratio at the Average Thickness (1.05 mil) and the 1, 2, and 3 Standard Deviation(0.24 mil) Points

Dry Film Thickness (DFT; mils)	Estimated Contrast Ratio
0.33	0.700
0.57	0.819
0.81	0.879
1.05	0.913
1.29	0.935
1.53	0.950
1.77	0.961

Table 3—Estimated Contrast Ratio at the Average Thickness (1.05 mil) and the 1, 2, and 3 Standard Deviation (0.24 mil) Points

Application Method	Spread Rate (ft^2/gal)	Wet Film Thickness (mils)	Dry Film Thickness (mils)	Estimated Contrast Ratio
Recommended	450	3.56	1.35	0.940
3 mil Bird	535	3.00	1.14	0.922
Rollout (average)	580	2.77	1.05	0.913
Rollout (pattern)	580	2.77	1.05	0.906

ness for each fractional area is used to generate a frequency plot, as shown in *Figure* 11. For most of the roller patterns examined, the results are well fit by a Gaussian distribution with varying averages and standard deviations.

Results of quantitative analysis aided by quantitative topography and visual imaging demonstrate that the ideal distribution of film thickness for maximized applied hiding is where even the thinnest film would deliver a contrast ratio of 0.98 or greater. *Table* 2 shows the estimated contrast ratio for the dried film thickness distribution, as shown in *Figure* 11, where the measured S/mil is 5.0, and the paint was not toned, retaining a Y reflectance of 94% and volume solids of 38%. Note the dramatic decrease in hiding as thickness decreases.

The estimated contrast ratios for different applications are shown in *Table* 3. Recommended spread rate, typical laboratory draw-down, and rollout tend to trend to thinner films, and thus lower hiding. For roller application, hiding is further lowered due to the pattern introducing thin spots. *Figure* 12 shows topography images comparing high-performance HEUR surface roughness and conventional HEUR with HMHEC surface roughness. The high-performance HEUR surface topography is more uniform in minimizing the thick and thin spots when compared to the conventional HEUR/HMHEC topography.

In addition to topography, time lapse imagery was used to understand how surface roughness changes as paint films dry. *Figure* 13 presents pictures of dried paint films using image analysis that shows the difference in pattern uniformity over a period of 10 minutes of drying at 72 ° F. How the topography of the film changes, or does not change, strongly influences how the dried film will appear. The two paints both have very rough surfaces at time zero, but paint 1 (utilizing a high-performance HEUR rheology modifier in combination with an HEUR ICI thickener) shows a significantly smoother film at 10 minutes after application. Paint 2 contains HMHEC and conventional HEUR technology. The image results clearly demonstrate that the initial pattern created by the roller cover is not necessarily the final pattern observed when the film is dry. Also, the time analysis demonstrated that a paint can flow and level once applied to the surface.

UNIVERSAL PERFORMANCE FROM WHITE TO TINT BASE

In addition to overcoming the need for sag or flow compromises common to traditional HEURs, the high-performance HEURs described herein were also designed to minimize viscosity loss on tinting, which is a common issue in deep bases. Incorporating viscosity retention upon tinting allows these high-performance HEURs to be used in formulation spaces where conventional HEUR technology cannot be used or has very limited utility. Medium, deep, and ultra-deep formulations require high colorant levels typically containing high concentrations of surfactants. The hydrophobes from these surfactants compete for adsorption sites on the latex particle surface and displace some of the thickener from the surface, resulting in a weaker network and lower viscosity. The surfactant also disrupts associations between thickener chains themselves, further contributing to viscosity decrease. Various approaches exist to mitigate

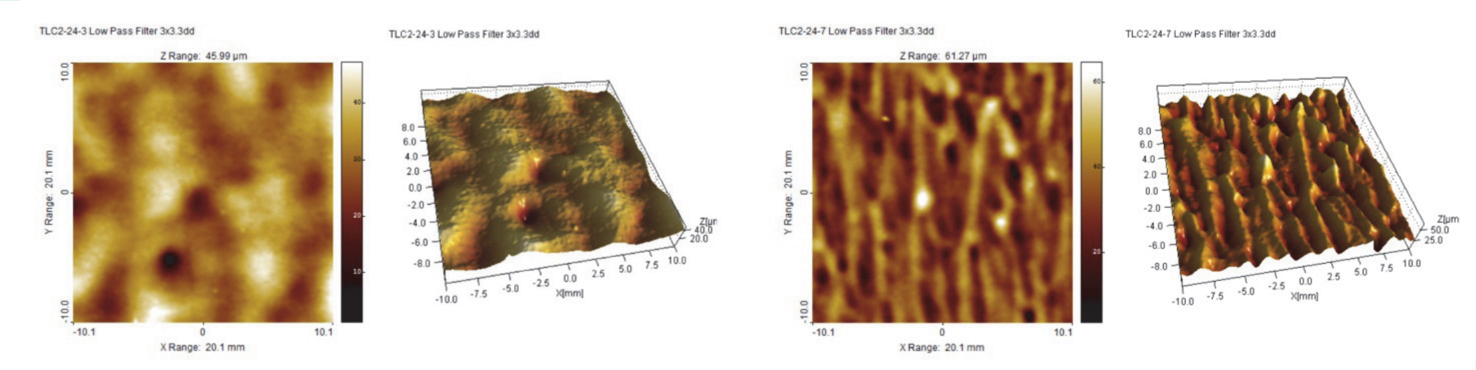

Figure 12—Topography images compare surface roughness of high-performance HEUR (left) and conventional HEUR with HMHEC.

these effects of colorant addition. The simplest approach is to minimize the use of associative thickeners and, in their place, use nonassociative thickeners such as hydroxyethyl cellulose (HEC). This approach tends to result in poor flow, a direct consequence of the volume-depletion flocculation mechanism by which nonassociative thickeners work. A second approach is to over-thicken the untinted base paint, so that after tinting, the viscosity drops to the desired final viscosity. This approach has a higher cost and is more difficult to handle during manufacturing because of the higher viscosity. Over-thickening will also lead to a range of final paint viscosities from a base because of the variation in tint amount and colorant type, which lead to wide variations in application performance and user experience.

A thickener that is tolerant of the surfactants in colorants would avoid both the viscosity loss on tinting and the issues with compensating for it. However, the composition necessary for colorant tolerance also creates strong self-association in water and, hence, an unpourable solution if the polymer is dissolved in water at 20% solids. By using an amine-containing hydrophobe and depressing the pH, a 20% solids solution of this thickener has a viscosity of only 2200 cP at pH 2.7, allowing for the new thickener to be of practical use for the current formulating needs. For example, in a 0 PVC/31 volume solids semigloss accent base with RHOPLEX™ VSR-1050 Emulsion that is thickened with either of the two conventional-structure HEUR KU-builders, the viscosity drop with 8 oz of red iron oxide or pthalo blue colorant was 30–40 KU (*Figure* 14). With the new thickener, the same colorants gave an increase of 4 KU upon tinting. The absence of viscosity loss in the tinted paint results in a KU (Stormer) viscosity of 130 vs 100 for the conventionally thickened paint. This higher mid-shear viscosity is reflected in higher Leneta sag resistance ratings, as shown in *Table* 4. Despite the significantly higher Stormer viscosity and sag resistance, the Leneta and brush flow offered by the new thickener are equivalent to those from the conventional thickeners.

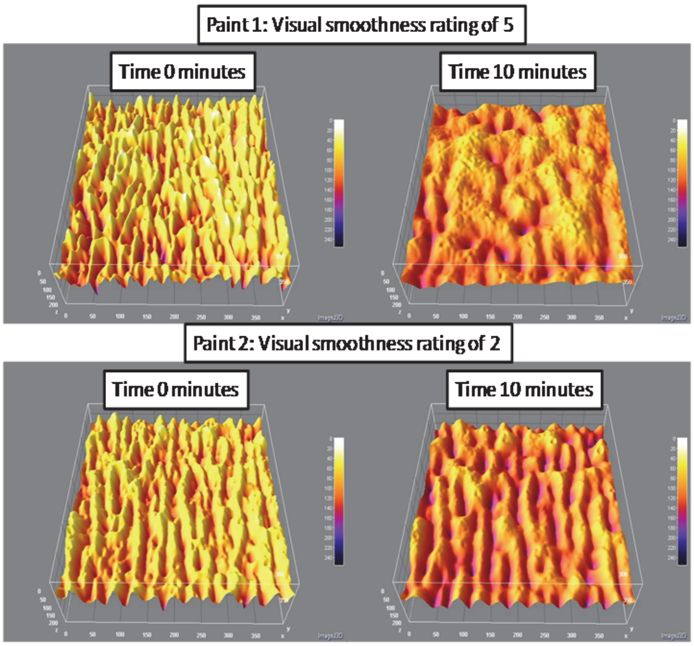

Figure 13—Topography of paint films during drying using high-speed photography correlates with the observed visual smoothness rating.

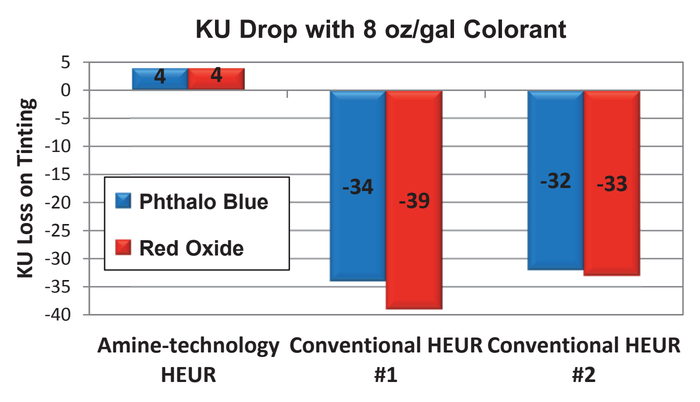

Figure 14—Viscosity loss on colorant addition in 0PVC/31VS semigloss accent base.

Table 4—Viscosity-Stable HEUR in Tinted 0PVC/31VS Accent Base with 8 oz/gal Colorant

	Conventional HEUR #1	Conventional HEUR #2	Amine-Technology HEUR
Blue-tinted paint			
KU viscosity	103	100	130
Blue sag resistance	14	10	24
Blue Leneta flow (10 max)	9	10	9
Blue brushed flow (10 max)	8	10	9
Red-tinted paint			
KU viscosity	98	99	130
Red sag resistance	12	8	20
Red Leneta flow (10 max)	10	10	9
Red brushed flow (10 max)	9	9	8

SUMMARY

The architectural coatings market continues to develop higher-performing paints to meet consumer demands of appearance, performance, and easy application to obtain a smooth, uniform finish with a minimum number of coats—whether it is an ultra-white or deep base. The most effective way to minimize the number of coats needed for an aesthetically pleasing finish is to maximize the applied hiding of the coating. A new associative rheology modifier technology based on HEUR chemistry has been described using ACID SUPPRESSION™ HEUR Technology. The technology uses amine functional hydrophobic groups resulting in HEUR polymers with a pH-triggered viscosity response. As a result, the associative thickening network can be turned on and off as a function of pH, thus facilitating product delivery in a solvent-free, low-viscosity aqueous solution without the need for VOC solvents or high surfactant levels. These hydrophobic amine groups can be present on the terminal HEUR polymer chain ends or along the HEUR polymer backbone. New hydrophobic amines have been designed and used to develop unique HEUR rheology modifiers that help deliver exceptional performance to architectural coating formulations. Most notably, performance features of KU builder products based on this new technology are helping to deliver a breakthrough level of sag/flow optimization, leading to more uniform film thickness, smoother surfaces, and higher applied hiding in white and pastel paints. With excellent viscosity retention on tinting, this technology offers breakout performance across a universal color spectrum.

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