DISPERSION PHASE DIAGRAMS

For HEUR-Thickened Acrylic Paint Systems

by **Tyler J. Bell** and **Raymond H. Fernando**,
California Polytechnic State University

and

Jason Ness, **Carrie Street**,
Karl Booth, and **Stephen Korenkiewicz**,
The Valspar Corporation

Latex paint formulations are highly complex aqueous dispersions containing latex, pigment, and filler particles in the dispersed phase, and a range of additives such as thickeners, surfactants, and dispersing aids in the continuous aqueous phase. The ability to predict the stability of these dispersions is a highly desirable, but difficult task. In this study, dispersion phase diagrams (DPDs) were constructed for four commercial paint formulations. A DPD is essentially a roadmap defining the good dispersion region and two different types of phase separation regions for a given paint formulation. The DPDs were constructed as a function of the concentration of two variables—an associative thickener and the external surfactant added to the formulations. The phase separated regions were determined via rheology and syneresis experiments. Each DPD was representative of a fully formulated, commercially available paint with the main components consisting of an all-acrylic latex; a combination of two hydrophobically modified, ethoxylated urethane (HEUR) thickeners; and a surfactant. Other variables included particle size of the latex and the nature of surfactant (nonionic vs anionic). This approach was found to be successful in determining highly reliable representations of the different regions of dispersion for each system. Another part of the study involved using contour plots of the physical properties of the wet and dry paint samples, which were excellent for observing trends in gloss, infrared backscatter (IRBS), viscosity, and conductivity caused by the surfactant, thickener, or latex used in the system.

INTRODUCTION

Hydrophobically modified, ethoxylated urethane (HEUR) associative thickeners, shown in *Figure* 1, are used in typical commercial paint formulations as rheology modifiers. The hydrophobes of these thickeners can associate in the aqueous phase to form various aggregates that can include surfactants commonly found in latex paints. In addition, they can adsorb onto a latex and other particles' surfaces.[2] HEUR thickeners have been used in the paint and coatings industry for over 30 years, and the rheology of these systems has been studied extensively in both aqueous solution and formulated paint systems. The use of these thickeners can lead to a good particle dispersion, which produces superior rheological and coating film optical properties.[3] However, associative thickeners are highly sensitive to the addition of most coating formulation components. Some key components include surfactants, pigments, and latex. Due to its amphiphilic nature, HEUR interacts with latex particles, pigments, fillers, surfactants, and solvents in the paint system. The contribution from all these components in the paint dictates the physical properties and the in-can stability of the paint which can lead to syneresis or phase separation.[3]

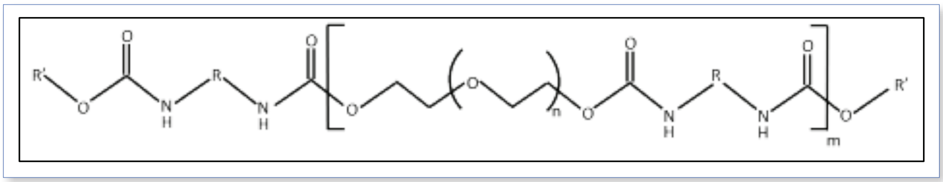

Figure 1—General structure of an HEUR associative thickener.[1]

Surfactants of different types and quantities are present for most architectural latex coatings. Even before the discovery of associated thickeners, surfactants were utilized, among many other reasons, for the stabilization of the bulk-dispersed phase (latex and pigment), wetting of substrates, and development of colorant strength.[4] In fully formulated coatings systems, surfactants do not function by themselves; instead, there are competitive and synergistic mechanisms that influence the system as a whole. For surfactants in water, aggregation occurs primarily as a result of the favorable hydrogen bonding of water molecules with other water molecules at the expense of interaction with hydrophobes from the surfactant.[4] These aggregates are called micelles, and they form above the surfactant's critical micelle concentration (CMC) that is specifically related to the chemistry of the individual surfactant molecule. This behavior of micelle formation can have a large influence on the viscosity and physical properties of coatings thickened with associative thickeners.[4]

Surfactants can provide nucleation sites to facilitate the hydrophobes from two different associative thickeners to build the viscosifying mechanism at low HEUR levels.[4] Surfactants, similar to HEUR, will adsorb onto latex surfaces via hydrophobic interactions between the latex surface and hydrophobes of the surfactant. The surfactant will compete with HEUR thickeners for adsorption sites onto latex particles, and the more hydrophobic the surfactant is, the more competitive it will be for adsorption onto latex.[5] In this study, two different surfactants were studied: one nonionic surfactant, an alkyl phenol ethoxylate (Surfactant A), and an anionic surfactant, an amine salt of an alkyl benzene sulfonate (Surfactant B).

Latex, typically synthesized via the process known as emulsion polymerization, is a dispersion made up of colloidal polymer particles in water. Emulsion polymerization is carried out in water with an emulsified monomer, surfactant, and initiator. The molecular weight (MW) of polymers synthesized with this method is typically high (1,000,000 g/mol or more is common).[6] This study focuses on latexes of acrylic polymer resins. Surfactants utilized in synthesis are very important in controlling the particle size and particle size distribution of latexes. Acrylic resins are the primary binders for most industrial coatings, with their best attributes being photostability and resistance to hydrolysis.[6]

There are two mechanisms to describe the stabilization of latex dispersions by surfactants. The first is by charge repulsion, in which the particle surface has an excess of one electrostatic charge (typically negative). For example, a latex is stabilized by an anionic surfactant wherein the hydrophobic portion (tail) is adsorbed onto the surface of the latex and the hydrophilic head group interacts with water.[6] This results in the surface of the latex particle being negatively charged, which causes electrostatic repulsion between latex particles. The second mechanism is commonly referred to as either steric, entropic, or osmotic repulsion, and can be introduced by adsorbed or covalently linked nonionic, water-soluble oligomeric species.[6] An example of entropic repulsion is when a nonionic surfactant anchors onto the latex particle via a hydrophobic interaction, and the hydrophilic portion extends into the water phase and attains a high degree of conformational freedom. As particles come closer together, the long hydrophilic regions are compressed, reducing the number of conformations possible in the system. This results in a loss in entropy. This resistance to the decrease in entropy leads to entropic repulsion.[6] Due to the reduction of the amount of water in the compressed particle surface layer, some literature refers to this mechanism as osmotic repulsion.[6]

The state of dispersion of colloidal particle systems used in paints has been studied for decades in an attempt to control their stability. Three types of dispersion quality and stability have been discussed in prior literature for latex-thickener mixtures. The first, which occurs at low levels of thickener levels, is called "bridging flocculation." The second is observed at very high levels of thickener or surfactant, and is called "depletion flocculation." The third is a good dispersion state observed at moderate thickener levels in which no flocculation is present.[7] These states of dispersion are governed by the many interactions present in the paint system.

Bridging flocculation occurs at low concentrations of polymeric thickener in a colloidal dispersion in which a single polymer chain adsorbs on two or more particles and "binds" them together.[8] The associating polymers can also create bridges

Table 1—Paint Formulation

Material Name	Amount (g)
Grind	
Water	6.30
Dispersant	0.49
Co-Dispersant	0.20
Defoamer	0.10
Dry TiO_2	21.89
Microbicide	0.16
Coalescent Aid	0.49
Water	7.33
Letdown	
Acrylic Resin	44.76
Defoamer	0.10
Water	14.01
High-Shear Thickener	0.00
Low-Shear Thickener	0.58
Water	3.60
Total Weight	100
%NVW – 44.8; %NVV – 34.0; PVC – 22.0	

Table 2—DPD Systems Described by Acrylic Latex and Surfactant

System	Acrylic Latex	Surfactant
1	A	A
2	A	B
3	B	A
4	B	B

through aggregation of several chains connected by the intermolecular associations of the polymer.[8] Flocculation by this method takes place only when the polymer chain is long enough to reach both particles (single strands or aggregated multiple polymer strands), and where the surface coverage by the adsorbed polymer is low. When the adsorption is reversible and the affinity of the polymer to the particle surface is weak, the polymer bridges are constantly forming, breaking, and then reforming again under no shear.[9]

Depletion flocculation can occur at relatively high concentrations of polymer when the associative interactions for the particle surfaces are weak. The flocculation mechanism is similar to that of a traditional thickener such as hydroxyethyl cellulose (HEC), which does not directly interact with particles in a typical coating formulation.[8] Depletion flocculation is the most widely observed type of flocculation, and is very common in traditional systems containing nonassociative thickeners.[5,10]

Depletion flocculation can also be introduced via surfactant additions to an HEUR-thickened system. When the particle surfaces of the system are covered mostly with surfactant, the system can enter a depletion flocculation state with the lack of polymer adsorption.[3] The free polymer in the system is excluded from the interstitial spaces in between particles, which creates an attractive force between the particles proportional to the osmotic pressure caused by the polymer concentration differential. When the volume concentration of the free polymer exceeds a certain limiting value, depletion flocculation is observed.[3] Depletion flocculation is dependent on the particle volume solids, thickener molecular size, and concentration.[1,5]

Dispersion Phase Diagrams

In an attempt to map out regions of flocculation and dispersion stability regions, Kostansek developed experimental techniques to generate phase diagrams for a relatively simple system containing latex, surfactant, and associative thickener.[5] An ideal dispersion phase diagram (DPD) that Kostansek developed is shown in *Figure* 2.[11] The overall study developed DPDs to illustrate the effect of latex particle size, composition, cosolvent, and electrolytes on dispersion stability. The testing method used relied heavily on microscopic examination of samples in which flocculation was observable. The objective of the work presented in this article is to construct similar DPDs for fully formulated commercial paint formulations.

The degree of pigment dispersion is of utmost importance, since it affects both the optical properties of dry films and rheological properties at wet stage of a fully formulated paint system. Typically, the degree of pigment dispersion is determined with the quick and simple fineness of grind test; however, the test is nonquantitative.[12] Many other techniques have been used to measure the degree of pigment dispersion for coatings; they include sedimentation techniques, chromatography, electron microscopy, light-scattering methods, contact microradiography, rub-out test, and color strength.[12] One of the light-scattering techniques, infrared back-scattering (IRBS), has been shown to accurately describe the pigment flocculation in dry and wet paint films. An IRBS study conducted by Balfour and Hird involved measuring the amount of IR radiation at 2500 nm that was back-scattered by a paint film at a given film thickness.[14] The resulting measurement of IR backscatter was correlated to the degree of TiO_2 flocculation in the dry film. The contribution of scattering by well-dispersed particles is low when compared to the increased scattering resulting from aggregated particles.[14]

Formulation Methodology

Four different acrylic paint systems were made with commercially available raw materials, following the formulation shown in *Table* 1. Each formulation contained the same basic HEUR-thickening package and surface-treated TiO_2. The targeted PVC and percent nonvolatiles by volume were 22% and 34%, respectively. The two variables that were changed were the all-acrylic latex and the surfactant (nonionic vs anionic). The two latexes and two surfactants used were: Acrylic A, a 105-nm particle diameter acrylic latex; Acrylic B, a 150-nm particle diameter acrylic latex; Surfactant A, a nonionic surfactant; and Surfactant B, an anionic surfactant. Surfactant A has an alkyl phenol ethoxylate structure with an HLB value of above 16, and Surfactant B is an amine salt of an alkyl benzene sulfonate. The four overall systems studied are shown in *Table* 2, with a detailed description listed below.

- System 1—Acrylic A (105-nm particle size) + Surfactant A (nonionic)
- System 2—Acrylic A (105-nm particle size) + Surfactant B (anionic)
- System 3—Acrylic B (150-nm particle size) + Surfactant A (nonionic)
- System 4—Acrylic B (150-nm particle size) + Surfactant B (anionic)

At least 25 samples (in some cases up to 40 samples) were made for each system with increasing concentrations of HEUR and surfactant, and a grid of samples prepared within a given system is shown in *Figure* 3. The physical properties of each sample analyzed were gloss, KU viscosity, and IRBS. Additional rheology and syneresis experiments were conducted to help conclude which type of phase separation was present in each sample. Contour plots of physical properties and DPDs were constructed using JMP® statistical software.

This paint preparation approach minimized batch–to–batch variability that occurs as a result of the paint-making process. These variables between each batch include temperature, pH, humidity, shear rate of mixer, and mix time.

Physical Property Testing

The KU viscosity of each paint sample was measured 24 hr after mixing. On sealed black and white contrast paper, 3 mil drawdowns were prepared, and after 24 hr, 60° gloss and the IRBS of the dry films were measured. The IRBS was measured on the black portion of the drawdown paper. The three properties (KU, gloss, and IRBS) were also plotted in contour plots with HEUR concentration (wt%) on the *y*-axis, surfactant concentration (wt%) on the *x*-axis, and one of the three physical properties on the *z*-axis. Construction of these contour plots allowed detection of trends for the given system of latex and surfactant. The contour plots were constructed using JMP statistical software.

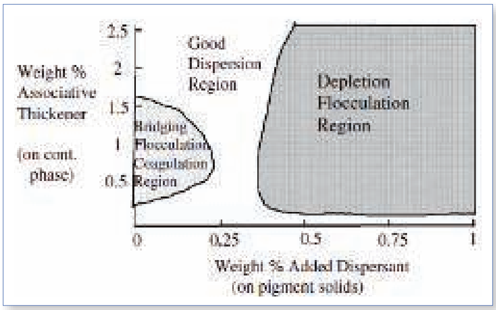

Figure 2—Idealized DPD showing the three possible regions for a simple system containing latex, thickener, and surfactant.[11]

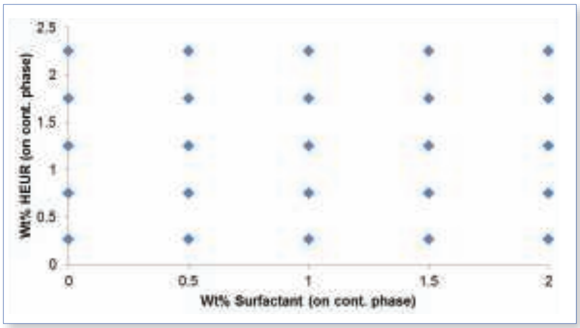

Figure 3—Graph showing the grid of samples made for System 1. Each point represents an individual sample that was created within the data set.

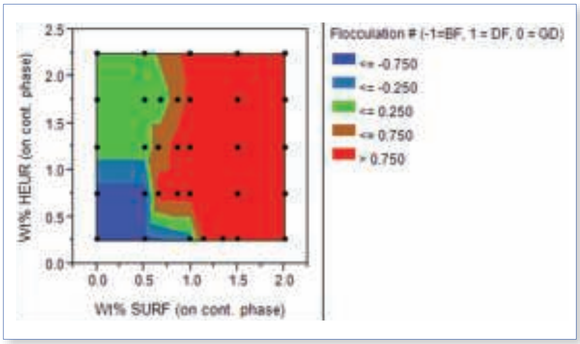

Figure 4—Contour plot example for the DPD for System 1 (Acrylic A and Surfactant A). (Blue region—bridging flocculation, red region—depletion flocculation, and green region—good dispersion.)

Viscosity Measurement Procedure

The rheological testing consisted of a shear-rate ramp from 0.1 to 1000 s^{-1}, with a 5% torque consistency tolerance to reach steady state and a maximum equilibrium time of 90 sec. The viscosity profiles were analyzed in viscosity vs shear-rate plots. The rheology testing starts with the paint sample at the lowest wt% HEUR and surfactant and moves sequentially left to right (*Figure* 3) with increasing surfactant content until the bridging flocculation region is no longer observed. The effect of the next level of HEUR is tested in the same way, and this process is repeated until an

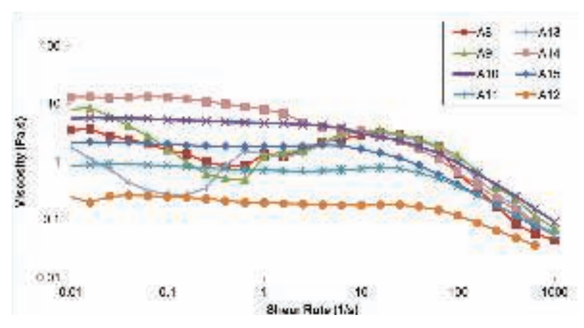

Figure 5—Shear-rate ramp results for System 2.

Table 3—Composition Description of Samples for *Figure* 5

Sample	Wt% Surfactant (on continuous phase)	Wt% HEUR (on continuous phase)
8	0.00	0.26
9	0.41	0.26
10	0.83	0.26
11	1.24	0.26
12	1.65	0.26
13	0.21	0.26
14	0.62	0.26
15	1.03	0.26

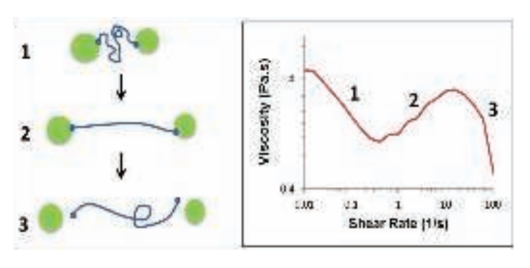

Figure 6—Schematic showing extension of bridge with respect to a bridging flocculation rheology curve containing a shear-thickening region.

HEUR level that does not show any signs of bridging flocculation is reached. The rheological analysis is conducted within two days of the preparation of the paint samples.

DPD Contour Construction

The dispersion phase diagrams (DPDs) are constructed in the form of contour plots. An example is shown in *Figure* 4. The contour is constructed in the JMP statistical software by simply assigning a value of –1 for bridging flocculation, 0 for good dispersion, and 1 for depletion flocculation. In some cases, the assigning of a flocculation number was not always clear due to the nature of the systems being studied. The transition between flocculation regions is a gradual change, and in some cases, tests exhibit signs that the sample is in the transition boundary of a flocculation region. To address this, a value of –0.5 would be assigned for a sample determined to be in the transition region between bridging flocculation and good dispersion, and a value of 0.5 for a sample in the transition region between good dispersion and depletion flocculation. The values were entered into the JMP statistical software and a contour plot was constructed for each formulation studied. This method is quite simple and effective in showing the transitions between regions.

RESULTS AND DISCUSSION

Rheology

As indicated above, viscosity versus shear rate testing was found to be a valuable tool in determining whether a composition has undergone bridging flocculation. The rheology data in *Figure* 5 shows the results for eight samples (System 2, which contains 105-nm diameter Acrylic A latex and anionic Surfactant B) at a fixed HEUR content (0.26 wt%) with different amounts (0 to 1.24 wt %) of surfactant. The composition of the samples for *Figure* 5 is shown in *Table* 3. The first three samples (A8, A13, and A9) with increasing surfactant concentrations (0, 0.21, and 0.41 wt%, respectively) had a region of shear thickening at intermediate shear rates, followed by a shear-thinning region at high shear rates. The shear-thickening region was absent for the fourth sample in the series (A14 with 0.62 wt% surfactant), although the viscosity curve is not smooth. The next sample (A10 with 0.83 wt% surfactant) has a broad low shear rate Newtonian region, and other samples having increasing levels of (A15 with 1.03, A11 with 1.24, and A12 with 1.65 wt% surfactant) showed Newtonian behavior at low and intermediate shear rates and shear thinning at high shear rates. The samples that exhibited shear thickening also exhibited syneresis (a clear liquid top-phase). The samples lacking the shear-thickening region had no phase separation. Similar observations with other systems studied established a strong correlation between syneresis and shear thickening. Thus, viscosity testing was employed as an additional tool to determine compositions undergoing bridging flocculation.

One of the most important factors controlling the rheology of the systems studied in this work is the affinity between the associative polymer chains and latex particle surface.[3] When the dispersion that has undergone bridging flocculation is placed under shear, the bridges are subjected to rapid extension, which can lead to high resistance to flow from the restoring forces present in the adsorbed bridges. The extended bridges can result in high resistance to flow if the adsorption to the particle is stronger than the applied shear stress.[3,9] This results in the shear thickening at intermediate shear rates, similar to what was observed for the samples A8, A9, A13, and A14. The remaining samples in the system are mostly Newtonian over the range of low to mid shear rates with a degree of shear thinning at higher shear rates, and they did not exhibit any shear thickening. The samples without shear-thickening regions were concluded to be in a good dispersion or depletion flocculated states, which were confirmed with syneresis experiments.

When high shear stresses associated with high shear rates are applied to a sample that has undergone bridging flocculation, the bridges are extended until they finally desorb from the particles. This is schematically represented in *Figure* 6. Since desorption occurs at a constant force, the system shows plastic flow at high shear rates (region 3 in the viscosity vs shear rate plot).[3,9]

Physical Property Analysis

Krebs unit (KU) viscosities of samples, measured 24 hr after their preparation, represented in four contour plots for each system, are shown in *Figure* 7. The KU viscosities are independent of the latex type; however, the type of surfactant has a significant influence. At low concentration, anionic surfactants cause higher viscosity losses.

Gloss Comparison

Gloss values measured at a 60° angle for each system are compared in contour plots shown in *Figure* 8. The 60° gloss plot for System 1 is the only plot that has the high gloss region correlating with the good dispersion region on the DPD (*Figure* 10). All the other systems (Systems 2, 3, and 4) only show correlation of gloss with relation to the amount of surfactant added to the system, and for these systems the gloss values do not translate to the good dispersion region of the DPD.

IRBS Comparison

The IRBS measurement results were plotted in contour plots for each system, and the comparison is shown in *Figure* 9. IRBS is a comparative measurement of the dry paint film in which lower IRBS values translate to the presence of better-dispersed TiO_2. The two Acrylic A (105-nm particle diameter) systems were observed to have a larger region of small IRBS values. The low IRBS value regions appeared to be correlated with the good dispersion regions of each DPD. This point will be revisited when the DPDs are discussed in more detail later.

DPD Comparison

The comparison DPDs for all four systems studied can be seen in *Figure* 10. Comparison of DPDs for Systems 1 and 3 with DPDs for Systems 2 and 4 indicate that the surfactant type has a significant influence on dispersion quality. The nonionic surfactant systems show a broader range of good dispersion regions at higher surfactant levels. The anionic surfactant yielded smaller good dispersion regions, with System 2 showing a good dispersion region from 0 to 0.4% surfactant and above 1.25% HEUR thickener level. The anionic surfactant has been shown to cause depletion flocculation at lower levels than the nonionic surfactant. The bridging flocculation region is also smaller for both the systems containing the anionic surfactant.

The influence of the latex can also be interpreted from the DPDs. From *Figure* 10, the top two DPDs are for the 105-nm particle diameter latex (Acrylic A), and the bottom two DPDs are for the

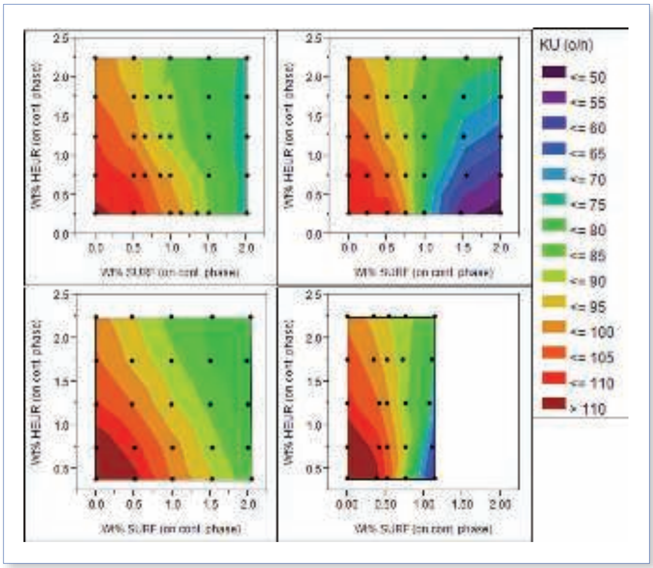

Figure 7—Twenty-four hour KU contour plots for System 1 (top left), System 2 (top right), System 3 (bottom left), and System 4 (bottom right).

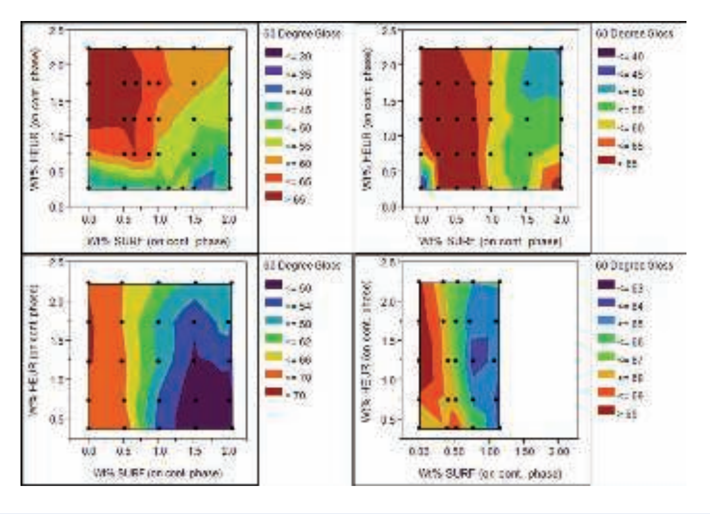

Figure 8—Sixty-degree gloss contour plots for System 1 (top left), System 2 (top right), System 3 (bottom left), and System 4 (bottom right).

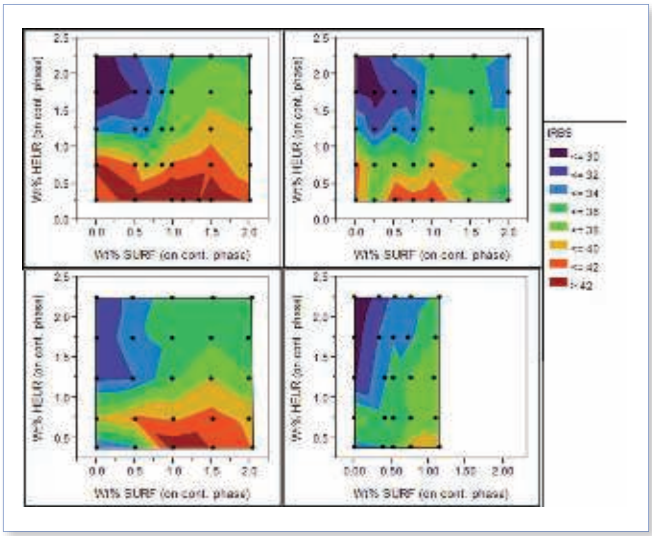

Figure 9—IRBS contour plots for System 1 (top left), System 2 (top right), System 3 (bottom left), and System 4 (bottom right).

150-nm particle diameter latex (Acrylic B). Acrylic A has more surface area per volume for adsorption of the thickener and surfactant onto the latex surface. The two systems containing Acrylic A have a significantly larger good dispersion region than the systems with Acrylic B.

The last observation to be noted is the relationship between IRBS contour plots and the DPDs. The low value IRBS regions appeared to be correlated with the good dispersion regions of each DPD. The testing methods of creating DPDs with rheology and syneresis experiments take one week to be completed. In comparison, the construction of IRBS contour plots takes only two days. For the systems studied in this project, the IRBS appears to the most efficient way for determining good dispersion regions.

CONCLUDING REMARKS

A DPD is essentially a roadmap to create stable new paint formulations, troubleshoot problematic formulations, and gain insights on interactions in a complex system. The simplicity of the DPDs allows interpretations of the main interactions of the system and how they affect properties of the coatings. The representation of DPDs in a grid fashion also allows statistical analysis and construction of contour plots. The DPDs are constructed utilizing common paint-making techniques, practically meaningful testing methods, and instrumental techniques commonly employed in the coatings industry, including rheometry and spectrometry.

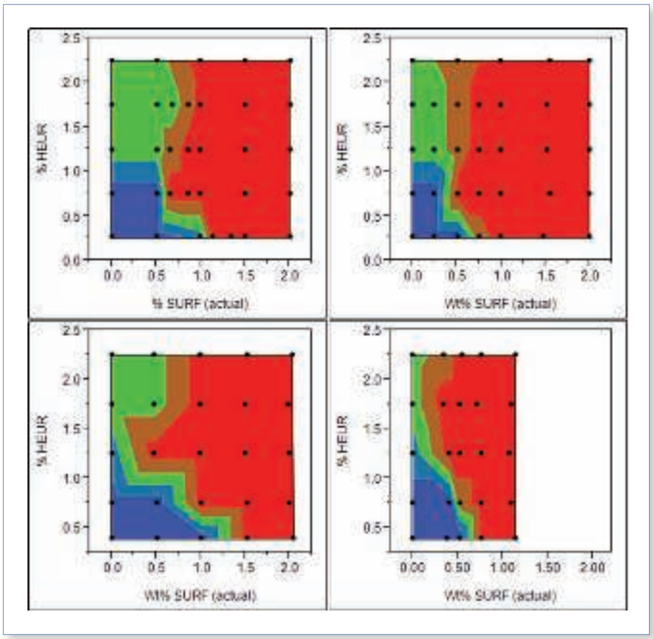

Figure 10—DPD contour plots for System 1 (top left), System 2 (top right), System 3 (bottom left), and System 4 (bottom right). (Blue region—bridging flocculation, red region—depletion flocculation, and green region—good dispersion.)

The effects of the vast range of rheology modifiers, surfactants, and other surface active agents on the dispersion stability and rheology of paint formulations are highly complex. It is well known to experienced formulators that extrapolation of fundamental learnings from simplified systems to fully formulated systems is a difficult challenge. The work presented here demonstrates for the first time the power of DPD concepts when applied to practical commercial paint examples. The techniques employed here provide a valuable tool for the paint formulator to affect formulation stability and material efficiency to save both time and cost in new formula development. As is evident from the DPDs discussed in this work, by formulating the paints within a broad but practical composition matrix, a formulator can clearly identify stable compositions and the boundaries of dispersion stability. More accurate determination of the boundary contours requires a logical next step that involves additional formulation work with compositions close to the DPD boundary regions. CT

References

1. Saucy, D., "Avoiding Viscosity Loss on Tinting." *Paint and Coatings Industry Magazine,* 35-38 (2008).
2. Chen, M., Wetzel, W.H., Ma, Z., Glass, J.E., Buchacek, R.J., and Dickinson, J.G., "Unifying Model for Understanding HEUR Associative Thickener Influences on Waterborne Coatings: I. HEUR Interactions with a Small Particle Latex," *J. Coat. Technol., 69* (867) 73-80 (1997).
3. Otsubo, Y., "Rheology Control of Suspensions of Soluble Polymers," *Langmuir, 11,* 1893-1898 (1995).
4. Mahli, D.M., Steffenhagen, M.J., Xing, L-l., and Glass, J.E., "Surfactant Behavior and Its Influence on the Viscosity of Associative Thickeners Solutions, Thickened Latex Dispersions, and Waterborne Latex Coatings," *J. Coat. Technol., 75* (938) 39-51 (2003).

5. Kostansek, E., "Using Dispersion/Flocculation Phase Diagrams to Visualize Interactions of Associative Polymers, Latexes, and Surfactants." *J. Coat. Technol., 75* (940), 1-8 (2003).
6. Wicks, Z.W. Jr., et al., *Organic Coatings Science and Technology, Third Edition*. New Jersey: John Wiley and Sons, 2007.
7. Olsson, M., Joabsson, F., and Piculell, L., "Particle-Induced Phase Separation in Mixed Polymer Solutions," *Langmuir, 21*, 1560-1567 (2005).
8. Horigome, M. and Otsubo, Y., "Long-Time Relaxation of Suspensions Flocculated by Associating Polymers," *Langmuir, 18*, 1968-1973 (2002).
9. Otsubo, Y., "A Nonlinear Elastic Model for Shear Thickening of Suspensions Flocculated by Reversible Bridging," *Langmuir, 15*, 1960-1965 (1999).
10. Kostansek, E., "Associative Polymer/Particle Dispersion Phase Diagrams III: Pigments," *J. Coat. Technol. Res., 3* (2006).
11. Kostansek, E., "Controlling Particle Dispersion in Latex Paints Containing Associative Thickeners." *J. Coat. Technol. Res., 4* (4): 375-388 (2007).
12. Hall, J.E., Bordeleau, R., and Rowland, R., "Quantifying Pigment Dispersion," *J. Coat. Technol., 60* (756), 49-61 (1988).
13. Rutherford, D.J. and Simpson, L.A., "Use of a Flocculation Gradient Monitor for Quantifying Titanium Dioxide Pigment Dispersion in Dry and Wet Paint Films," *J. Coat. Technol., 57* (724), 75-83 (1985).
14. Balfour, J.G. and Hird, M.J., "Flocculation—Its Measurement and Effect on Opacity in Systems Containing Titanium Dioxide Pigments," *J. Oil Col. Chem. Assn., 58*, 331-344 (1975).

AUTHORS

Tyler J. Bell,[a,b] **Raymond H. Fernando**,[a] **Jason Ness**,[b] **Carrie Street**,[b] **Karl Booth**,[c] and **Stephen Korenkiewicz**[c]—(a) Dept. of Chemistry and Biochemistry, California Polytechnic State University, San Luis Obispo, CA, 93407; (b) The Valspar Corporation, Minneapolis, MN, 55415; (c) The Valspar Corporation, Wheeling, IL, 60090; rhfernan@calpoly.edu.