INTRODUCTION

As new coating formulations are being developed to comply with increasingly stringent environmental constraints, application properties are still expected to be maintained or improved over previous performance standards. This poses major challenges to both raw material suppliers and coating formulators globally. To tackle this problem, coating formulations and raw materials must continually be innovated as new regulations are introduced. For example, as VOC levels are reduced through formulation changes and new zero-VOC products are introduced, additional surfactants are often supplemented to help improve the stability of the paint. These complex surfactant combinations have subsequently influenced the defoaming needs in modern coating formulations. Specifically, defoamers that were once effective are no longer acceptable for the elimination of macrofoam during manufacturing and microfoam formation during the final application of a film. To address these new technical challenges, more efficient defoamers must be produced that do not contribute to the total VOC content or adversely affect other performance properties.

To produce these more efficient defoamers, the basic drivers of foam formation and destabilization (defoaming) must be understood. Briefly, in pure liquids like water, no foam formation occurs as the bubbles quickly rise and burst at the air/water interface. In formulated systems, however, surfactants are present and consequently stabilize air bubbles through the creation of foam lamellae at the air/water interface (Figure 1). Additional information on the fundamental principles of foam formation and stabilization has been extensively reviewed elsewhere and is outside the scope of this article.1-4
With the understanding that foam formation will inevitably be present in all paint formulations, the question to address is how can we efficiently remove it? To better understand this, the standard compositions of defoamers and their modes of action will be examined briefly. Compositionally, formulated defoamers are made from three key ingredients:

1. The carrier liquids: glycols, water, mineral and silicone oils, and other organic liquids;
2. Emulsifiers and wetting agents: surfactants, hyperbranched polymers;
3. Tertiary or active components: hydrophobic solids, modified silicones, fatty acids, and proprietary materials.

Breaking this down further, the carrier liquid can be water, but most commonly is a water-insoluble low surface tension liquid that individually acts as a defoamer and also serves to transfer hydrophobic particles to the lamella interface (Figure 2, Entering). The emulsifiers control the degree of emulsification of the defoamer in the water phase and play a crucial role in the entry and spreading rate of the hydrophobic particles into the lamella (Figure 2, Spreading). Finally, the tertiary components can boost defoaming activity and improve the defoamer’s stability/compatibility (Figure 2, Rupture of Lamella). This mechanism outlines some of the fundamental principles required for a defoamer to efficiently function, but other interactions also exist in the defoaming mechanism. More thorough reviews have previously described other mechanisms and modes of action and can be found in these references.1-4

Although a plethora of technical knowledge is readily available about the physics of foam stabilization and destabilization, substantially less information is shared on the standard test methods used to evaluate defoamers.1-4 Furthermore, virtually no data is available on how critical formulation attributes can synergistically or antagonistically influence a defoamer’s perceived effectiveness. With this in mind, we first looked at two common defoaming test methods used in the architectural coatings market.

Specifically, these methods simulate the critical points of foam generation, manufacturing, and application foam formation. For processing or manufacturing foam where a large amount of air is incorporated into the paint, either the shaker or dissolver test methods are implemented (see Experimental section). Roller or brush methods are used to evaluate application defoaming properties. Within the scope of this article, only the shaker and dissolver methods were evaluated, as similar studies are currently being performed on the application defoaming procedures.

RESULTS AND DISCUSSION

For this work, a standard semigloss zero-VOC acrylic paint formulation was used (Table 1). Paints were made in the absence of defoamers and rheology modifiers to allow for their post-incorporation

Table 1—Standard Acrylic Formulation 758-63 of a Semigloss Zero-VOC Paint

<table>
<thead>
<tr>
<th>Formula 758-63</th>
<th>Raw Material</th>
<th>Weight (lb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grind</td>
<td>Water</td>
<td>120</td>
</tr>
<tr>
<td></td>
<td>Low shear thickener</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Dispersant</td>
<td>7.5</td>
</tr>
<tr>
<td></td>
<td>Wetting agent</td>
<td>3.13</td>
</tr>
<tr>
<td></td>
<td>TiO2 powder</td>
<td>225</td>
</tr>
<tr>
<td></td>
<td>Extender</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>Defoamer</td>
<td>5.53</td>
</tr>
<tr>
<td>Let Down</td>
<td>Water</td>
<td>149.38</td>
</tr>
<tr>
<td></td>
<td>Coalescent</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>Acrylic latex</td>
<td>450</td>
</tr>
<tr>
<td></td>
<td>Hollow polymer</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>Wetting agent</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>Ammonium hydroxide</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>High shear thickener</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>Mid shear thickener</td>
<td>8</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>1112.0</td>
</tr>
</tbody>
</table>

Figure 2—The mechanism of a defoamer as it enters, spreads, and ruptures the foam lamella.
using the same paint; this eliminated any batch–to-batch variability. The incorporation of the defoamer post-addition (0.5%, see Experimental section) did not contribute to increased air content in the paint prior to air incorporation.

In our initial study, we wanted to determine the variables in the shaker method that contributed to defoamer performance variability. This type of information is crucial, as it gives the formulator a better understanding of how to best distinguish performance improvements between products.

The first variable tested was how the duration of shaking would affect air incorporation. Samples were placed on the identical spot (outer edge) of the shaker and shaken in increasing time increments to determine if a maximum amount of air could be incorporated into the paint (Figure 3a). The linear correlation of air incorporation versus time indicates that no maximum % air was achieved up to 15 min and, for practicality, samples were not shaken longer than 15 min. We also evaluated how quickly the density of a sample should be measured after the completion of the initial shaking step. As expected, it was observed that the % air decreased (increased density) with increasing time. However, in this formulation, the rate of air loss was relatively slow—less than 1% in the first hour (Figure 3B). While it is recommended to measure the density directly after shaking, this data suggests that delays on the order of minutes will not impact the accuracy of the test substantially.

In a similar manner, we set out to determine some of the key variables in the dissolver test method. The two variables evaluated were RPM speed and shear time. It was found that with 4 min of shear, reliable data could only be generated at speeds less than 3000 RPM (Figure 4a). Higher speeds resulted in the generation of heat, which would affect the testing.
decreased the paints’ viscosity and consequently resulted in faster air removal. In a similar fashion, heat generation occurred if a sample was subjected to shear (2000 RPM) for a time longer than 4 min (Figure 4b). These examples nicely highlight the importance of establishing the procedural limitations of this method. Fundamentally, if the temperature of paint rises over a critical value, the corresponding decrease in viscosity will inherently improve the perceived performance of a defoamer.

For the remainder of this work, we followed the shaker and dissolver methods outlined in the Appendix. The conditions used for the dissolver method did not result in any heat generation for the samples evaluated. Although the purpose of a defoamer in a formulation is clear, we wanted to gain some insight as to how other formulation attributes, namely rheology, influence a defoamer’s effectiveness. This was evaluated in the shaker and dissolver test methods by making a series of paints with either a fixed mid shear viscosity (98 KU) and variable high shear viscosity (1.1–2.2 ICI) or constant ICI (1.5) and variable KU (85–110). Rheology curves of the low shear and high shear regions were also generated to show the differences between the low and high shear regions in the paint (Figure 5).

Interestingly, linear correlations were observed in both the shaker and dissolver methods. Specifically, when using the shaker method, as the KU increased, the % air (defoaming efficiency) improved (Figure 6a), while no correlation was observed at the variable ICI levels (Figure 6b). However, the opposite phenomenon was observed when evaluating the samples using the dissolver method. The linear correlation only existed when the ICI levels increased (Figure 7b), while no trend was visible at the various KUs (Figure 7a).

These rheological effects can be explained by looking into the shear levels applied during the application tests. Specifically, the shaker method incorporates air via a low shear process and subsequently the low shear character of the paint determines how much air gets incorporated. The same logic applies to the dissolver method, although this time the high shear rheology of the paint dictates the quantity of incorporated air. This demonstrates how other factors can directly influence the perceived effectiveness of a defoamer depending on the application test and rheological loading levels of the paint.

At this point, we have shown some of the key variables when performing defoaming methods and how small rheological differences in a formulation can directly influence air incorporation. Taking into account this information, we can reduce the overall error and substantially improve our ability to determine the individual effectiveness of new defoamers. Specifically, the use of polymeric defoamer actives has successfully been utilized to improve the overall performance of defoamers, with one unique class being the hyperbranched materials. These materials are synthesized via the addition of epichlorohydrin
(ECH) with ethoxylated alcohols under controlled conditions. Initially, the alkoxylate reacts with ECH to form the alkyl epoxide. This epoxide further ring opens in the presence of additional alkoxylates and subsequent chain extension continues until the epoxide conversion is complete. Upon completion, this process results in the formation of hyperbranched polymers whose hydrophilicity and hydrophobicity can be optimized around the needs of a given paint formulation (Figure 8).

With a clear mechanistic understanding of how the polymerization process occurs, we can begin evaluating how other physical characteristics influence defoaming performance. As a general rule, the defoamer must walk a fine line between being compatible/incompatible in the system, and this balance can be controlled systematically through the introduction of hyperbranched polymers.

In this study, a series of experimental hyperbranched polymers were synthesized from the same ethoxylated alcohol with the only compositional variable being the molecular weight. It would be expected that by fine-tuning the molecular weight, the mobility of the polymer can be optimized to exhibit an optimum defoaming performance. Four samples were synthesized with increasing molecular weights (Figure 9a) and were compared against the leading star-shaped defoamer benchmark using the shaker method (see Appendix). Only data from the shaker test has been presented, because similar trends can be measured with the dissolver method. It was observed that as the molecular weight increased, the defoaming efficiency for the star-polymer decreased. Specifically, an optimization of the molecular weight allowed for an improvement of >25% in defoaming efficiency over the benchmark star-polymer (Figure 9b).

Independently of the polymers’ molecular weight, the degree of hydrophilicity also influences defoaming efficiency by aiding in the defoamers’ emulsification into the paint. This means that by synthetically controlling the hydrophilic/phobic balance of the hyperbranched polymers, we can control defoaming efficiency. To evaluate this, four hyperbranched polymers were synthesized with increasing hydrophilicity (Figure 10). It was observed that an optimum balance of hydrophilicity was generated with Star 2. Star 1 was too incompatible (hydrophobic), while the higher hydrophilic contents in Star 3–4 made the polymer too compatible with the system and consequently defoaming performance decreased. This highlights the importance of being able to control the degree of emulsification when using emulsifiers in defoaming formulations, and how correctly optimized hyperbranched polymers can substantially improve a defoamer’s performance.

CONCLUSIONS

Even though foam generation and stabilization in water-based systems has been extensively studied, ever-evolving formulations and increasingly stringent regulatory constraints challenge the efficiency of existing defoamers in the next generation of architectural formulations. To prepare solutions for these challenges, having proficient formulation expertise combined with the ability to create new polymeric additives allows for the unique opportu-
nity to develop defoamers with improved defoaming efficacy across a vast range of challenging coating formulations. Specifically, a series of defoamers was evaluated using standard test methods where the influences of other formulation parameters on defoaming performance are typically not accessed. We demonstrated, using an architectural coating formulation, how multiple rheological factors independently influence defoaming efficiency based on the test method used. A careful review of both the high shear and low shear rheology levels should be considered when evaluating the effectiveness of defoamers, especially when comparisons are made with different paint batches. Taking into account these observations, we further demonstrated how recent advancements in star-shaped polymers can minimize foam stabilization in increasingly restrictive paint formulations.

**APPENDIX: Procedures**

**Shaker Method:** A 150 g sample of paint (Table 1) was weighed into a half-pint paint can. The defoamer was then added at the desired percent weight (0.5%) based on the total weight of the paint (150 g). A low shear mixer (Servo Dyne, Digital Mixer) equipped with a propeller blade was used to incorporate the defoamer into the paint for 5 min at 500 RPM. The low shear was used to avoid the premature addition of air into the paint. The can was then placed on the outer edge of a Red Devil Shaker clamp (farthest from axis of rotation) so that maximum arc was achieved and shaken for 5 min (cans must be placed in the identical location). Immediately after shaking, the weight/gallon of shaken paint was determined. The decrease in density compared with that of the unshaken control paint sample was regarded as the amount of foam generated.

\[
\text{Air Content (\%)} = \frac{A - B}{A} \times 100
\]

\(A = \text{wt/gal unstirred}\)

\(B = \text{wt/gal stirred paint with defoamer}\)

**Dissolver Method:** A 150 g sample of paint (Table 1) was weighed into a half-pint paint can. The defoamer was then added at the desired percent weight (0.5%) based on the total weight of the paint (150 g). A low shear mixer (Servo Dyne, Digital Mixer) equipped with a propeller blade was used to incorporate the defoamer into the paint for 5 min at 500 RPM. The low shear was used to avoid the premature addition of air into the paint. The can was then placed under a dissolver (Dispermat LC-55-E) equipped with a toothed dissolver disc (lightweight propeller blade #50) followed by shearing the sample for 3 min at 3000 RPM. Immediately following, the weight/gallon of the stirred paint was determined. The decrease in density compared with that of the unstirred control paint sample was regarded as the amount of foam generated.

\[
\text{Air Content (\%)} = \frac{A - B}{A} \times 100
\]

\(A = \text{wt/gal unstirred}\)

\(B = \text{wt/gal stirred paint with defoamer}\)

**Rheology Curves:** All samples were performed with a Haake MARS 3 (Thermo Scientific) rheometer fitted with a 35 mm, 2° cone and plate spindle at a temperature of 25°C. A pre-shear of 100 sec\(^{-1}\) was applied for 5 sec before the sample was allowed to recover for 30 sec. A forward shear ramp was then performed from 0.01–2800 sec\(^{-1}\) over 2 min.

**References**


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