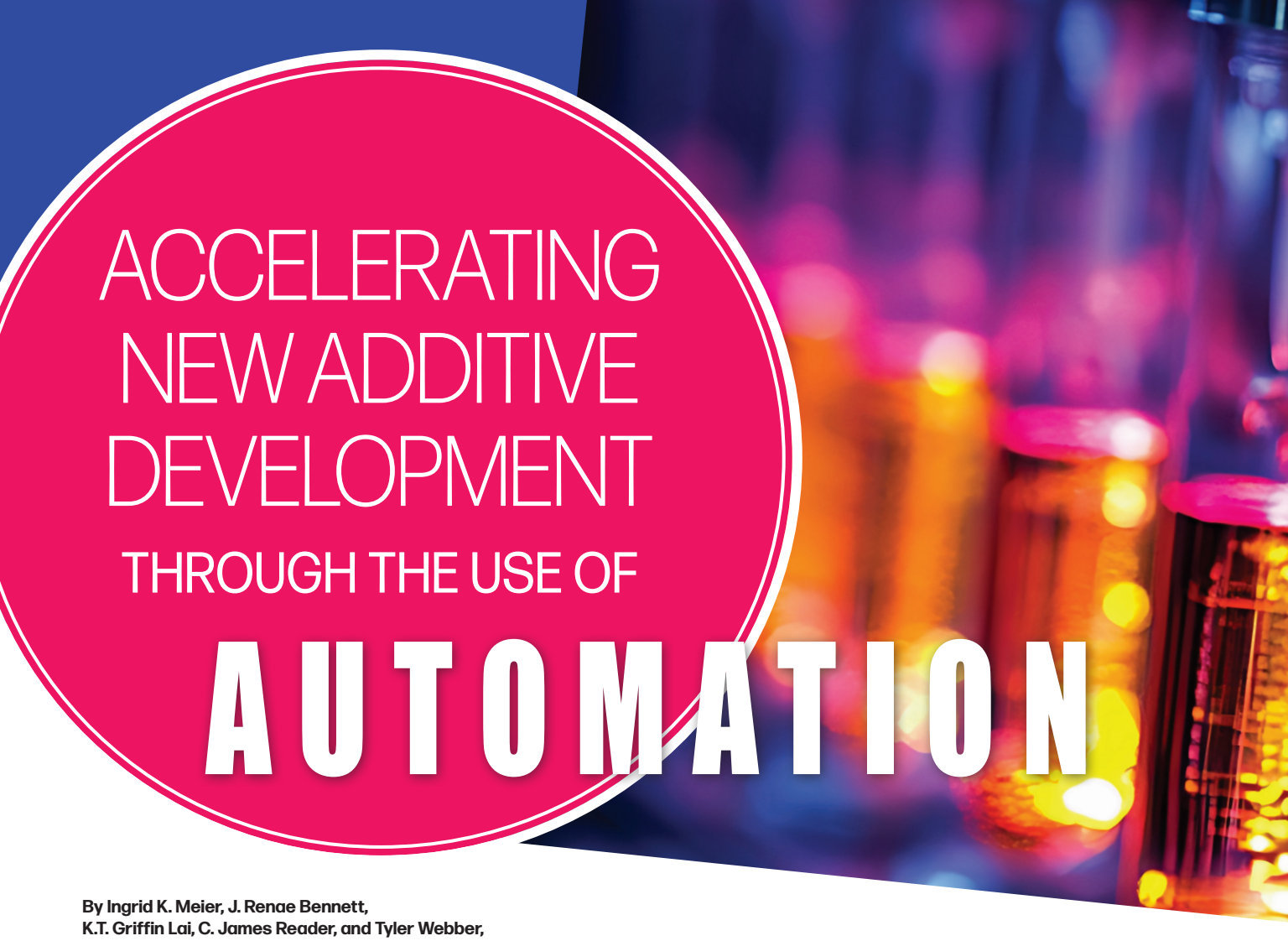
ACCELERATING NEW ADDITIVE DEVELOPMENT THROUGH THE USE OF AUTOMATION



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Many additives used in waterborne coatings and inks are complex formulations. For example, most defoamers are comprised of insoluble oils, compatibilizers, and, oftentimes, hydrophobic solids and surface-active species. Since their mechanism of action involves delivering incompatible droplets capable of spreading across and rupturing foam lamellae, it is important to balance this incompatibility with the equally critical requirement that the defoamer not cause defects or recoatability issues in the cured film. Additionally, it is important that the formulated additive resist phase separation under typical transportation and storage conditions. The objective of this article is to share specific details of how a project team developed unique automated test methods and used them, in combination with design of experiments, to accelerate the development of new defoamers and deaerators. Case studies in which the team optimized silicone polyether structures, as well as formulated defoamers, for both performance and stability will be discussed.

Introduction

Approximately 15 years ago, a "voice of the customer" survey was conducted to better understand unmet market needs in coatings and inks. One of the primary challenges formulators identified was that of finding the ideal additive to mitigate foam-related complications in a brand-new formulation, particularly after most other system components had already been established. Therefore, rather than try to develop new defoamers targeted to solve specific foam control problems in select formulations, the team chose to design a series of defoamers that spanned the entire performance space—ranging from strong, incompatible grind defoamers to very compatible defoamers required for low viscosity coatings intolerable of defects. Ideally, the set of defoamers would be designed in a structured manner so that each defoamer's performance would be predictable relative to the others, thus, enabling formulators to more quickly home in on a suitable solution. However, to accomplish this goal it would be necessary to build a deep understanding of the structure-performance relationships of several key components used to create defoamers, specifically, the silicone polyethers, surfactants, and hydrophobized particles.

An automated liquid handling formulator capable of preparing multiple-component mixtures in batches of 48 samples was used to create formulations that could then be used in subsequent evaluations. To further build upon the increased number of prepared samples, an automated testing laboratory focused on surface science was built to accelerate these evaluations. The core of this automated laboratory consisted of testing platforms to automatically measure dynamic surface tension and turbidity, as well as to assess foam behavior following a shake test. Although originally intended to prepare and evaluate formulated surfactants in applications such as electronics

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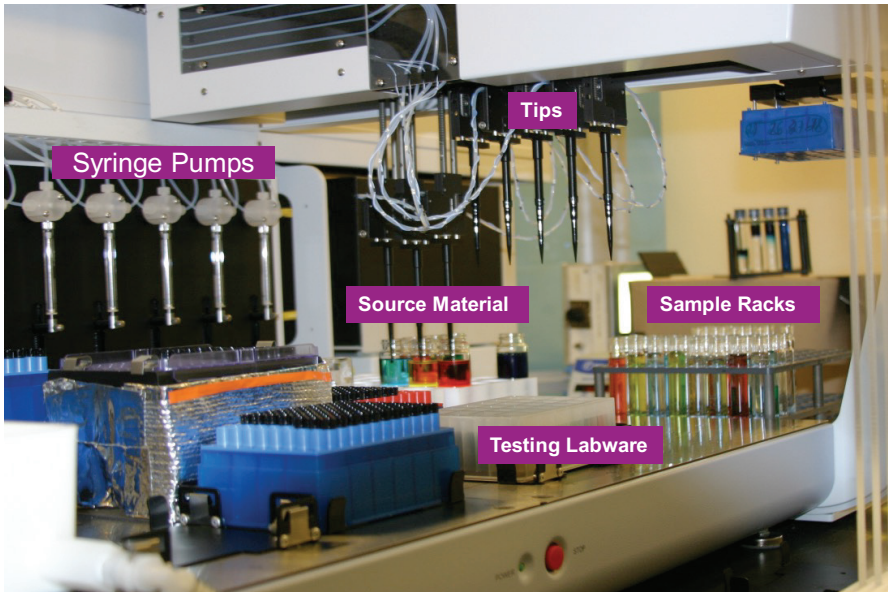
and cleaning, the operator in charge of the system recognized the potential for its broader use. Other automated techniques were then added to the surface science and automation laboratory to develop defoamers and deaerators more efficiently.

Experimental

Automation Equipment and Test Procedures

A JANUS G3 automated liquid handling workstation (PerkinElmer/Revvity) that can dispense a combination of up to eight different materials was used to prepare 2-5 mL formulated aqueous samples for future characterization (**Figure 1**). Typically, the individual test tubes were arranged in a rack on the

FIGURE 1
Automated liquid formulator.



deck of the formulator and, after filling and capping each tube, the rack of 48 samples was mixed on a vortex mixer.

To further utilize the capabilities of the formulator, an air sparge test was developed to take advantage of the controlled dispense feature of this equipment. Using this protocol, a set volume of air was delivered at a set flow rate into each sample. A Bassler high-speed camera was mounted to capture images before and after the air sparge (**Figure 2**). Images were captured over a set period, and then analyzed to quantify the amount of foam bubbles generated and how long the foam persisted. Each image was sliced into samples and analyzed using a proprietary technique developed for this purpose. The data could then be graphed to represent foam generation and decay over time. Data could also be compared along with reference to each sample's initial turbidity and the density of the foam layer over time; this provided a more complete picture of each additive's ability to prevent and control foam.

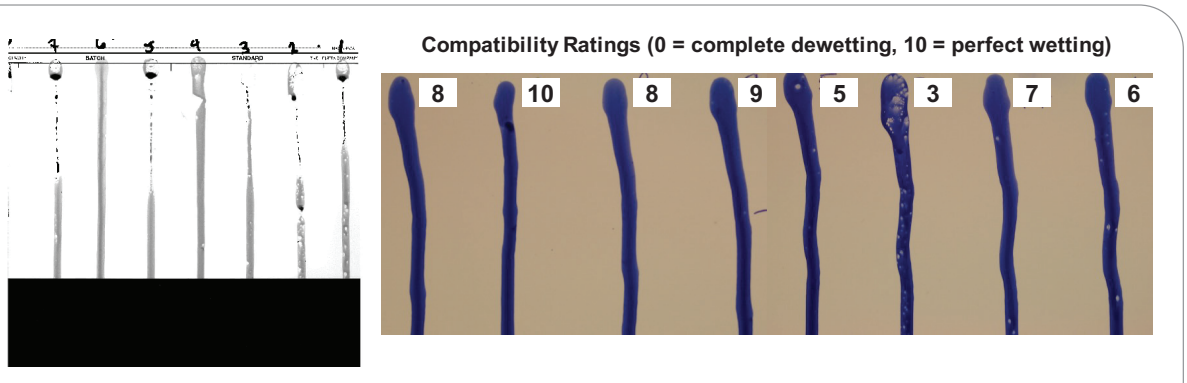
Another technique developed around the capability of the Janus formulator involved a multi-dispense of liquid onto a Leneta chart. For example, an aqueous resin could be diluted with water to achieve a low enough viscosity for testing; addition of an oil soluble blue dye enabled greater visibility of foam and incompatibility within the formulation. The Janus formulator was used to add set amounts of different defoamers to vials containing 2 mL of dyed resin and the set of samples was mixed using a vortex mixer. The resulting formulated resin systems were then automatically dispensed using individual syringes, four at a time, by aspirating approximately 0.7 mL of liquid and dispensing it at the top of a Leneta Form 5C chart that was mounted at a 45° angle. The dispensed liquids were allowed to flow down the chart, after which the dried strips of coating were examined. This "dropdown" test method demonstrated good reproducibility and directly correlated with results from a manual draw down to assess compatibility. An early sample dropdown test chart is shown in **Figure 3**. Results were assessed visually and each defoamer's compatibility in each resin system would be rated on a scale of 0-10, with zero representing complete dewetting and 10 representing excellent compatibility with no visible craters or dewetting.

Three SITA t-100 maximum bubble pressure tensiometers (SITA Lab Solutions) were mounted in parallel and used to measure dynamic surface tension of each sample at bubble frequencies of approximately 0.1 through 10 Hz. A UR10e Cobot, programmed to move a 24-well plate, enabled sequenced testing to be conducted using the three tensiometers at the same time.

A foam shake test platform included a homemade hydraulic apparatus that quickly moved sample tubes back and forth at a 180° arc for several seconds. This automated method of foam generation and quantifiable measure of its collapse was developed to correlate with the time-consuming Ross Miles Foam Test (ASTM D1173) and to replace manual foam shake tests that had poor reproducibility and caused ergonomic problems for those conducting them. The UR10e Cobot removed capped sample tubes from the storage rack and placed three individual sample tubes into a holder for the hydraulic shaker. The Cobot then returned to its home position while waiting on its next command. A camera mounted at the foam shake platform took an initial image before shaking and then captured subsequent images for a pre-determined time after shaking. After they had been shaken, the Cobot returned these samples to their rack and then moved to retrieve and set up the next three samples to repeat the foam

FIGURE 2
High-speed camera images of four 2-mL aqueous samples during the air sparge testing using the automated formulator (left) and an example of foam density analysis for one of the samples after air sparging was completed (right).

FIGURE 3
Early automated dropdown test charts showing effects of defoamer incompatibility.



shake test. The data generated from the air sparge and foam shake methods created a unique perspective into the performance of each additive. While both methods look at foam generation and foam decay over time, the resulting data could differ dramatically depending on the chemical composition of the additive studied.

An entire series of 48 formulations could be evaluated for both dynamic surface tension and foam shake behavior within two hours—a task that would have taken a technician at least 20 times longer to perform by hand.

A LUMiSizer® Dispersion Analyzer (LUM GmbH) that uses STEP-Technology® (Space and Time-resolved Extinction Profile) was used to compare the relative stabilities of formulated defoamers. This instrument was helpful in studying the tendency of various hydrophobized particles to settle out over time, and results could be used to screen materials for settling and anti-settling behavior in the early design phase as well as to predict long-term shelf stability of fully formulated defoamers later in the product development process.

Evaluation of Silicone Polyethers (SPEs)

The first set of SPE prototypes were each diluted to 20 wt. % in a C12-15 alkyl benzoate with low viscosity (<50 cPs at 25 °C), and the diluted SPE solutions were added at 0.1, 0.2, and 0.3 wt. % to the wood stain and masonry sealer formulations described in **Tables 1** and **2**, respectively. The wood stain formulation in **Table 1** was prepared by adding the ingredients together and then mixing for 20-30 minutes using an overhead mixer to prepare an ~1 kg masterbatch that could be used for post-adding defoamers for testing.

The masonry sealer formulation in **Table 2** was prepared by adding the ingredients together and then mixing for 20–30 minutes using an overhead mixer to prepare an ~3 kg masterbatch that could be used for post-adding defoamers for testing. The pH and viscosity of the masterbatch was adjusted by adding additional ammonia and/or thickener to bring it into typical range.

Results and Discussion

The design and selection of the silicone polyethers (SPEs) to be used in this new line of defoamers and deaerators was the team's first challenge. Initial design spaces were mapped out based on the generic silicone polyether structure shown in **Figure 4** and considering compositional ranges in which freedom to operate had been established based on an extensive prior art search. Two initial designs of experiments (DOE) were created, one to target molecules within this

TABLE 1
Wood Stain Formulation

Component	Wt. %
Acrylic polymer dispersion vehicle	50.1
Water	44.0
80% 2-dimethylamino-2-methyl-1-propanol (aq.) – *add slowly to neutralize the resin dispersion above*	1.0
The three colorants below were combined separately under continuous agitation, adding more water to achieve acceptable viscosity before adding the combined mixture to the polymer dispersion above	
Black (6C11B704) colorant	0.6
Yellow (6C11B243) colorant	3.0
Red (6C11B143) colorant	1.3
TOTAL	100.0
Diluted SPEs were added to the masterbatch and mixed for 20 minutes. *Typical coating viscosity: 12.1 mPa-s (Brookfield, spindle 2, 60 rpm)* *Typical coating properties: 19.6 wt. % non-volatile, pH 7.4, 59.1 g/L VOC*	

TABLE 2
Masonry Sealer Formulation

Component	Wt. %
Water	37.3
100% Acrylic, self-crosslinking emulsion binder, T_g = 55 °C, 41% solids	58.2
Low foam dynamic wetting agent	0.9
Siloxane surface control additive	0.1
Dipropylene glycol n-butyl ether	1.2
Propylene glycol phenyl ether	1.0
Plasticizer	0.8
Ammonia	0.1
HEUR thickener	0.4
TOTAL	100.0
Diluted SPEs were added to the masterbatch and mixed for 20 minutes. *Typical coating viscosity: 142 – 175 mPa-s (Brookfield, spindle 2, 60 rpm).* *Typical coating properties: 26.3 wt. % non-volatile, pH 8.8 – 9.2, 96.1 g/L VOC.*	

FIGURE 4
Silicone polyether (SPE) structure.

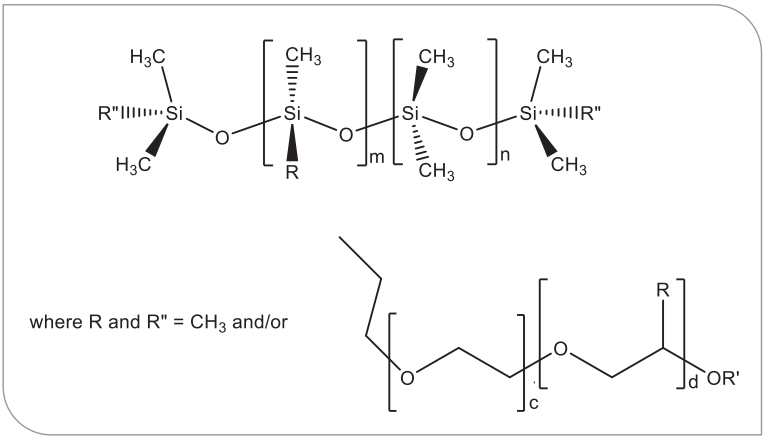


FIGURE 5
Example design space for a DOE-like that used to identify initial SPE structures.

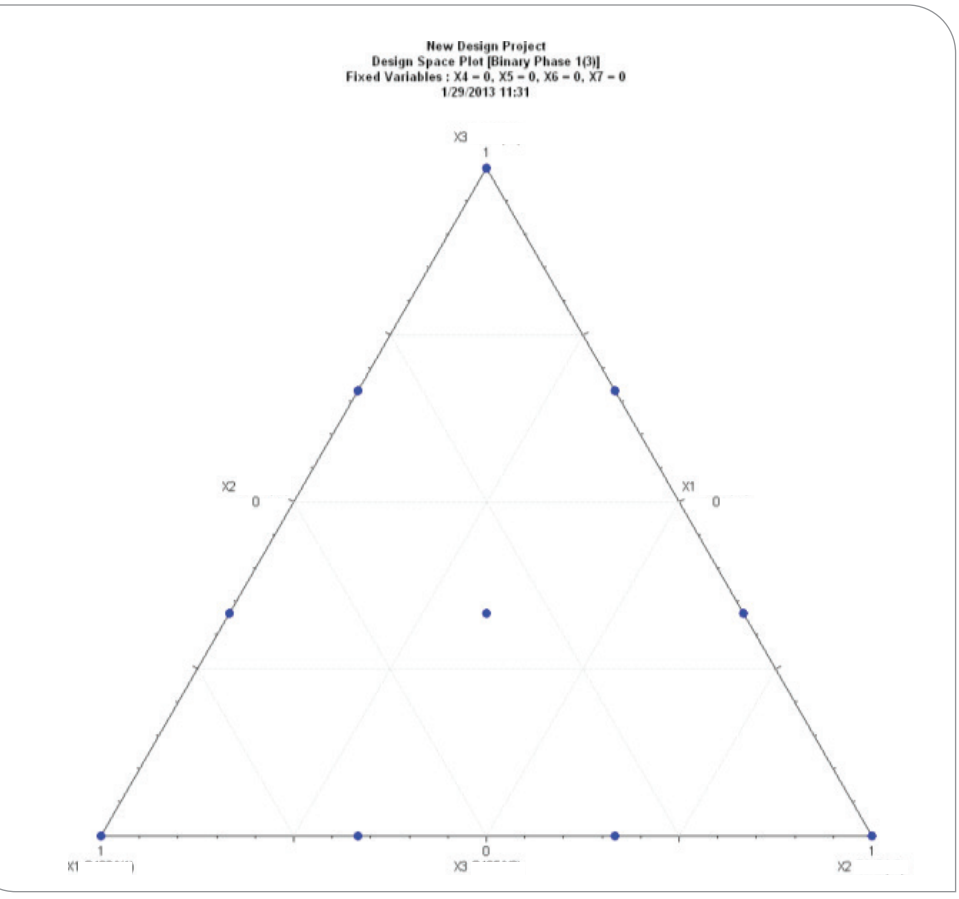
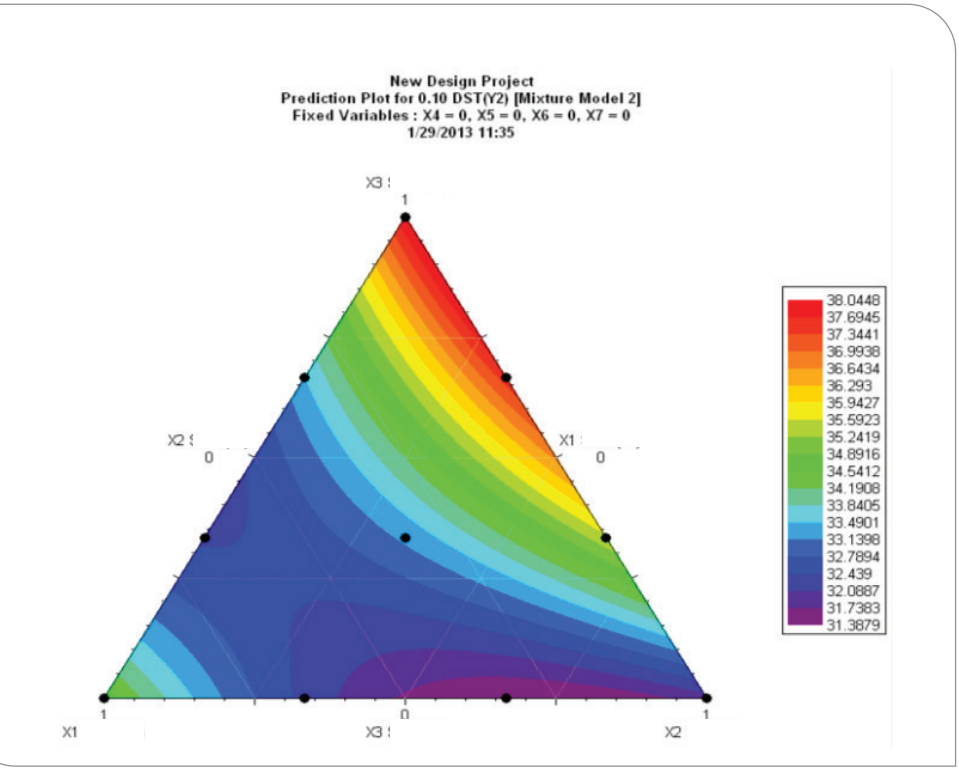


FIGURE 6
Heat map for a mixture DOE designed to predict the optimal composition needed to achieve the lowest dynamic surface tension at 0.1 wt. % in water.



space expected to perform as defoamers to control macrofoam and the other to target structures expected to perform as deaerators to control microfoam. This approach then required the team to synthesize the initial 18 SPEs representing various compositions within each design space. An example DOE is shown in **Figure 5**, where each vertex of the ternary plot represents a maximum relative concentration of polydimethylsiloxane, polyethylene oxide, and polypropylene oxide, respectively. After measuring properties of the 10 initial SPEs within this DOE, a heat map like that shown in **Figure 6** was constructed by the software to highlight compositional spaces predicted to have the optimal structures needed to achieve the best performance for a given metric. Future work was then focused on refining the compositions within this narrower design space.

Once the first sets of SPEs had been prepared, the team needed to characterize them with regards to their defoaming and deaerating strength and relative compatibility in relevant coating formulations. Full applications testing of all the unformulated SPEs would have been extremely time consuming. The new defoamers would need to be optimized for a dozen different formulations including a pigment dispersion, packaging ink, wood stain, masonry sealer, two overprint varnishes, gloss metal topcoat, and parquet wood, rust-conversion, plastic, and two architectural coatings. Therefore, the team decided to use automated screening methods for quickly screening the foam control behavior and compatibility of the SPEs to help narrow the search for the ideal SPEs.

The wood stain and masonry sealer formulations (**Tables 1** and **2**) containing various levels of diluted SPE were evaluated using the automated formulator to conduct air sparge testing as described above (**Figure 7**). In this way, the behavior of each of the initial SPEs could be evaluated with regards to its ability to control foam created via air sparge. Additionally, imaging of the formulated coatings containing the SPEs was performed using the automated foam shake test apparatus to characterize the ability of the SPEs to control foam generated in this different manner.

Finally, the automated formulator was used to perform the dropdown test with each formulated wood stain and masonry sealer, and each stripe of dried film was

evaluated for signs of foam and dewetting. In this way, the results of the initial SPE DOEs could be used to create narrower DOEs to further identify the optimal SPE structures to be used to create the formulated defoamer prototypes. One SPE was chosen for its deaeration properties and four SPEs that performed as defoamers were selected. Multiple DOEs were then used to determine the optimal defoamer compositions needed for each of the target application spaces: 1) mill bases and high pigment-volume concentration (PVC) architectural flat paints, 2) colorants and semi-gloss paints, 3) printing inks, 4) wood coatings and clear coats, and 5) automotive and plastic coatings.

A deep understanding of surfactant structure-property relationships had already been built within the team thanks to previous years of work in this field during which the automated formulator and dynamic surface tension and foam testing had been invaluable. Therefore, selection of the components needed to provide wetting and molecular defoaming was straight forward.[1-3] However, selection of the appropriate hydrophobic particles and understanding the best means of incorporating them to create the most stable defoamers became the next challenge.

The LUMiSizer® Dispersion Analyzer was used to gain further insight into the tendency of various hydrophobic particles to settle out of the liquid phase and helped the team assess the relative stabilities of formulated defoamers and deaerators. The ability to evaluate 12 samples in a single experiment under different centrifugation speeds, time periods, and temperatures accelerated the team's ability to understand the behavior of the particles and select final defoamer compositions that resisted phase separation. Using this approach, ideal hydrophobic particles were identified to provide additional defoaming strength as well as anti-settling benefits in the defoamer formulation. When the defoamers were scaled up in production, the effectiveness of particle incorporation could also be assessed by studying the resulting defoamers using the LUMiSizer®.

Several unique automated test methods were developed to specifically address some of the most labor intensive and ergonomically challenging aspects of screening components needed to create and launch a series of seven new defoamers and one new deaerator within two years.

While the use of the automated test methods described here certainly accelerated the project team's ability to develop the targeted series of defoamers and deaerators, it would be misleading to neglect to mention some of the limitations of these automated methods. In particular, the liquid formulator could not be used to add solids or accurately dispense viscous liquids, and the foam test methods could not be used with viscous formulations. Coating formulations with high pigment loadings tended to coat the walls of the sample tubes preventing useful imaging analysis. The development of automated applications testing protocols was not undertaken because it would have required far more time and money to do so than to simply perform the traditional testing in a manual fashion. Moreover, the inability to sufficiently use such methods often enough in the future would have made their return-on-investment poor. By accepting these limitations and focusing on developing automated test methods that could repeatedly be used to save the most time and operator pain, the team was successful in speeding up the SPE screening process to leave more time in the schedule for conducting full applications testing on the most promising defoamer prototypes.

Conclusions

Several unique automated test methods were developed to specifically address some of the most labor intensive and ergonomically challenging aspects of screening components needed to create and launch a series of seven new defoamers and one new deaerator within two years. Additionally, a fundamental understanding of the structural features of silicone polyethers that contribute to defoaming and deaeration, as well as system compatibility, was built. The knowledge gained through this work continues to fuel the team's new additive and automated test method development. ❊

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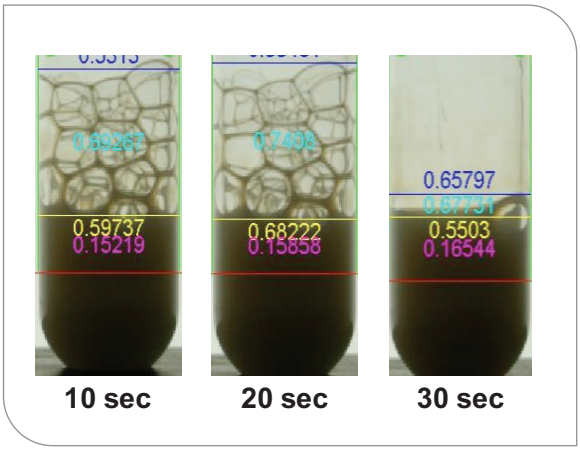

FIGURE 7 Images of defoaming within a formulated wood stain after air sparge.

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