



Development of High Throughput Method for Evaluating the Effect of Additives on Foam Stabilization in Clear Coatings

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One of the more challenging aspects of formulating water-based coatings is in the selection of a foam control additive package and evaluating its effect on the ability of the formulation to resist and release entrained air. Current laboratory methods of analyzing defoaming efficiency can be complicated, time consuming, and typically require significant volumes of materials for testing. The novel method presented here allows for small volume, high throughput analysis of the effect of foam control additives and other surfactants on the ability of a coating formulation to resist air entrainment. The method additionally allows for use of “shear rate” and “time of recovery” as process variables that can be used to simulate a diverse range of conditions that a coating may experience during the manufacturing or application process. Furthermore, the unique approach of using color as a comparative tool to evaluate the relative amount of air in the liquid coating formulations is shown to be an effective means of analysis.

INTRODUCTION

Formulation of paint and coatings is an important process used to improve properties of liquid coatings during manufacturing, storage, and application. Formulation can also have a significant effect on the performance properties of the dry film. One of the more challenging aspects of formulating water-based coatings is in the selection of the foam control additive (FCA) package. Part of the challenge lies in the fact that both defoamers and deaerators for waterborne coatings work by being slightly incompatible with the binder system. The balance of FCA and binder interaction needs to be matched carefully, as an FCA that is too incompatible will cause severe dry film defects while an FCA that is too compatible will not effectively remove air from the coating. Further complication can be caused by other surfactants introduced into the system that may inadvertently cause foam stabilization.

Current laboratory methods of analyzing defoaming and air release efficiency can be complicated, time consuming, and typically require significant volumes of materials for testing. Many current methods rely on introducing air into the liquid coating material by bubbling or injecting air into the solution and then evaluating the behavior of the air in the solution. While these methods offer value and key fundamental understanding, they do not have the benefit of being able to examine the performance of the coating formulation in a high shear environment, such as during the manufacturing or application process.

The method described here introduces the ability to incorporate air into the coating solution across a variety of shear ranges, to quantitatively measure the effect of air incorporation

into the solution, and to record the rate of air leaving the solution. Furthermore, the method allows for evaluating the efficacy of the FCA over time and repeated insults.

BRIEF DESCRIPTION OF FOAM CONTROL ADDITIVES

Foam control additives for waterborne coatings are commonly divided into two distinct categories: defoamers and deaerators. In the most general terms, these additives function by aligning to and destabilizing the foam lamella. It is commonly understood that the function of a defoamer is to destroy macrofoam at the liquid–air interface. Deaerators are commonly thought to function by displacing foam-stabilizing surfactants, therefore promoting diffusion of air into the liquid medium, reducing the size of the microfoam to the point of complete dissolution. In practice, it is often difficult to truly differentiate between the two additive types. Most often, formulators will select a defoamer or deaerator based on visual observation of the foam type, macro versus micro. Evaluation of the efficacy of the additive will also be made via visual inspection of the bulk liquid and the dried film.

CONVENTIONAL HIGH SHEAR DEFOAMER EVALUATION METHOD

A common laboratory method that is used to simulate a coatings exposure to high shear, such as in a production environment, involves comparing the density of the coating before and after subjecting the coating material to a controlled shear environment. Commonly, a density difference is calculated for each formulation as follows:

$$\Delta\rho = \rho_i - \rho_f$$

$\Delta\rho$ = Density difference

ρ_i = Initial density (before shear)

ρ_f = Final density (after shear)

Density difference values can be calculated for each formulation and then compared. Lower $\Delta\rho$ values can indicate a formulation that shows better defoaming efficiency under these test conditions.

Figure 1 shows a workflow that describes this method using a high speed disperser to create shear. The shear environment can be controlled between formulation samples by using consistent mixing time and mixing shaft RPM. Density measurements can also be taken across a longer time scale to measure that ability of the formulation to release air over time.

The advantage of the process shown in Figure 1 is that it is a relatively easy test to perform with equipment common to paint and coatings laboratories. This process also has the advantage of being able to vary the shear

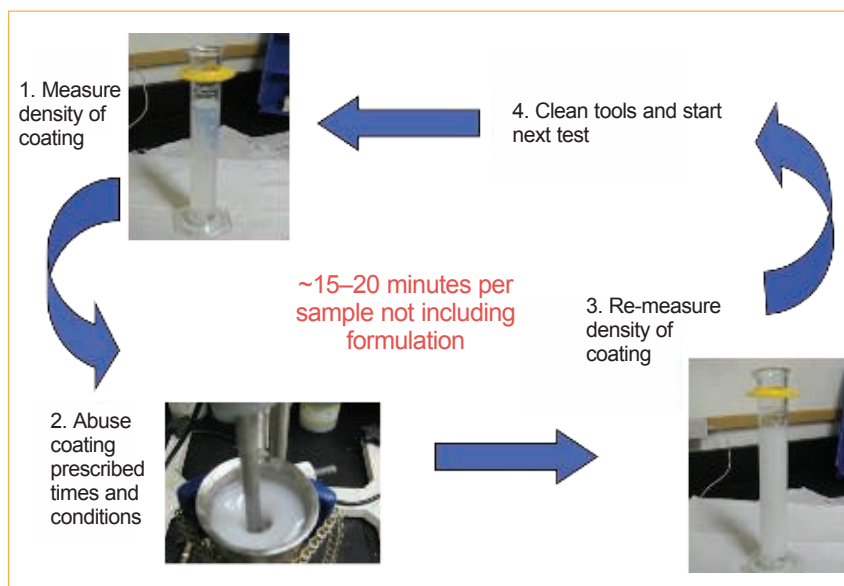


Figure 1—Conventional FCA analysis workflow.

applied to the formulation, and offers the ability to measure air release over time. The disadvantages are that this test usually requires large amounts of liquid coating for each measured formulation (typically in excess of 100 g), the necessity of disturbing the coating (pouring from one container to another during the process of measuring density) which may affect the air entrained in the coating, as well as the length of time required to perform each test.

LOW SHEAR METHODS

There are a variety of methods that are based on injecting air bubbles into the coating material in a low shear method similar to ASTM D1173. These methods offer an excellent opportunity to understand the fundamental effects of foam collapse and stabilization. There is, however, the disadvantage of not being able to examine the functionality and efficacy of FCAs in high shear, abusive environments that many coating formulations will experience during either manufacturing or application.

EXPERIMENTAL DESIGN AND SAMPLE PREPARATION

The method developed here is part of a larger additive formulation study that evaluated the effect of a variety of additives on the performance of Dow's experimental natural oil polyol (NOP) polyurethane dispersion (PUD), QRX-1821NCS. For this original study, a design of experiments (DOE) was developed using the following constraints:

- Six FCA packages at two levels
- Five surface wetting additives at two levels
- Four surface/slip additives at two levels
- Control: QRX-1821NCS with no additives
- Constants: PUD, solids, viscosity before additives

The DOE was reduced to 176 experiments and used two 96 well plates, with eight controls in each plate, for the FCA analysis portion of the study. Liquid samples were prepared using a high throughput formulation robot. Formulations were transferred to 1 ml vials, commonly known as parallel pressure reactor (PPR) vials. The PPR vials, as shown in *Figure 2*, were each loaded with 0.50 ml of formulation and 0.5 g of ceramic beads used to increase shear on the coating material.

PROPOSED HTR WORKFLOW—PICA II

The goal of this project was to create an HTR workflow that mimicked conventional high shear methods. *Figure 3* shows the proposed workflow of this method. The first step is to capture an original, unadulterated image of the formulation. Step two uses a “wrist shaker” that mechanically shakes the vial at a controlled speed over a specified time. These variables can be manipulated to simulate a range of quasi-shear conditions on the liquid sample. The final step is to capture an image of the shaken vial. During this last step, multiple images can be captured to evaluate air release over time. Various types of media can also be added to each formulation to facilitate an even higher shear environment during the shaking step. Images taken before and after shaking can be

Table 1—Experimental Settings

Instrumentation Control	Value
Wrist shaker speed	5
Wrist shaker time	30 sec
Time between images	60 sec
Number of images	10

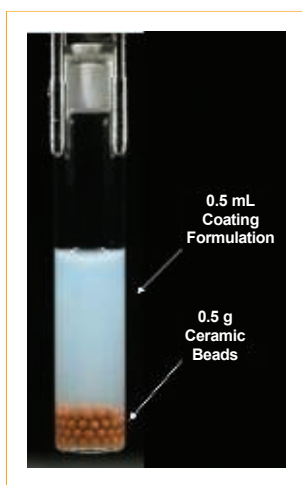


Figure 2—Image of loaded PPR vial.

compared to determine the effect of the additives on the formulation in this environment. Experimental settings for this workflow are listed in *Table 1*.

IMAGE ANALYSIS

The images were analyzed using custom image analysis software.* Acquired images of the vials were loaded into the software and analyzed for color of the solution. The software calculates color values in a user defined area of the image. Values were then exported to a spreadsheet as CIE $L^*a^*b^*$ color values, where L^* describes the white–black color balance, a^* the red–green, and b^* the yellow–blue. These values can then be used to compare the color difference between two measured images using CIE 1976 $L^*a^*b^*$ formulation to calculate the total CIE $L^*a^*b^*$ color difference, ΔE^1 :

$$\Delta E = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$$

$$\text{Where } \Delta L^* = L^*_1 - L^*_2, \Delta a^* = a^*_1 - a^*_2, \Delta b^* = b^*_1 - b^*_2$$

Small ΔE values indicate small changes in color.

RESULTS AND DISCUSSION

High Throughput Defoaming Method: Proof of Concept

Initially, it was expected that foam height would be measured in the PPR vials as a proxy for density measurements. As can be seen on the left side of *Figure 4*, initial testing of a PUD with no additives showed minimal foaming as well as no discernible change in liquid height. The addition of ceramic beads, as shown on the right

*Image analysis software developed by Dow Chemical Company.

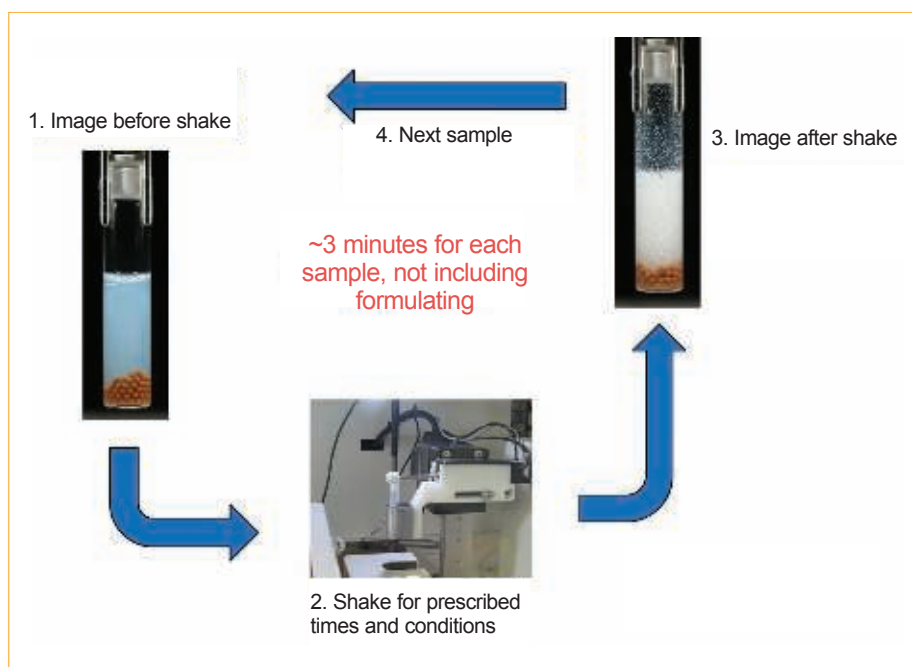


Figure 3—HTR defoaming workflow.

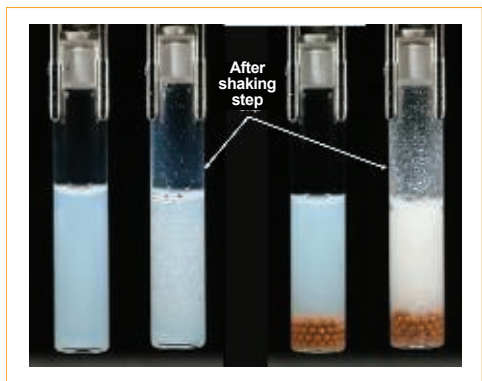


Figure 4—Effect of using ceramic beads.

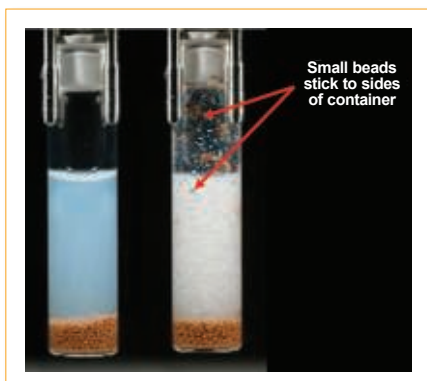


Figure 5—Effect of small beads on image quality.



Figure 6—Benefit of using colored beads.

side of *Figure 4*, increased the shear applied on the liquid sample during the shaking step and facilitated the incorporation of air but still did not significantly affect the height of the liquid formulation. Fundamentally, it is hypothesized that the addition of the beads creates a highly turbulent mixing environment that increases the rate of air incorporation into the liquid phase. Additionally, it is thought that the shear created by the beads can possibly approximate the mechanical abuse liquid coatings may experience during some manufacturing and application processes. It was also revealed that the weight of the individual beads affected the quality of the images, as shown in *Figure 5*, where smaller, lighter beads tended to stick to the sides of the PPR vials instead of returning to the bottom after being shaken.

The ceramic beads selected for this study are round Zirconox milling media available from Jyoti Ceramics. The beads are rare earth stabilized, tetragonal zirconia, polycrystal ceramic with diameters ranging from 1.0–1.2 mm. In some cases, as shown in *Figure 6*, even the larger beads did not return to the bottom of the vial. In this case, the color of the Zirconox media has a distinct advantage over similar products, which are typically white or clear in color, in that it is relatively easy to identify images that may give false color values due to the presence of a variant bead.

Measurement of Liquid Height as a Proxy for Density

As discussed previously, the intent of this method was to measure differences in liquid height as a proxy for changes in density. Because of the small diameter of the PPR vials, surface tension effects and rheology of the liquid formulations significantly affect material flow rate on interior sides of the vials. Examples of two different formulations are shown on the top and bottom of *Figure 7*. The images are aligned so that the picture furthest to the left

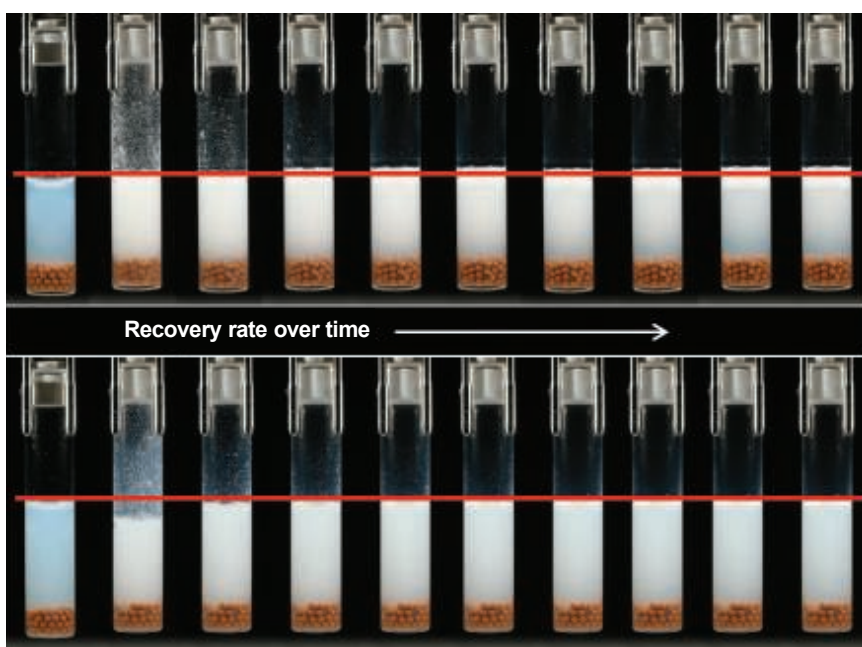


Figure 7—Liquid height recovery over time.

is taken prior to shaking. Additional images were taken at one minute intervals to capture the defoaming effect over time. The series on top shows an increase in liquid height with a maximum at approximately three minutes, while the series on the bottom shows a decrease in liquid height with a steady height state reached at approximately three minutes.

The challenge in using the liquid height measurement is two-fold. The first is how to resolve the relevance of the directionality of the liquid height change. The second is that this method is not able to statistically resolve a recovery rate. As can be seen in *Figure 8*, although the before and after images have similar liquid heights, suggesting that the formulation has returned to its initial state, it is obvious there is still entrained air in the liquid phase.

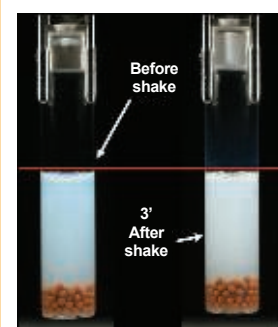


Figure 8—Lack of resolution in height measurement.

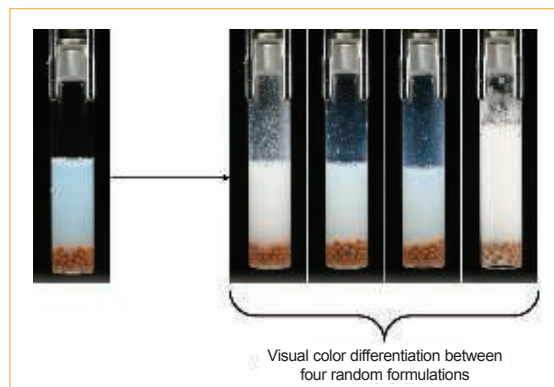


Figure 9—Examples of color differentiation due to air entrainment.

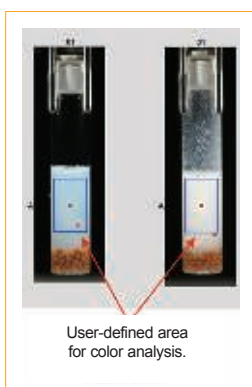


Figure 10—User-defined area for color analysis.

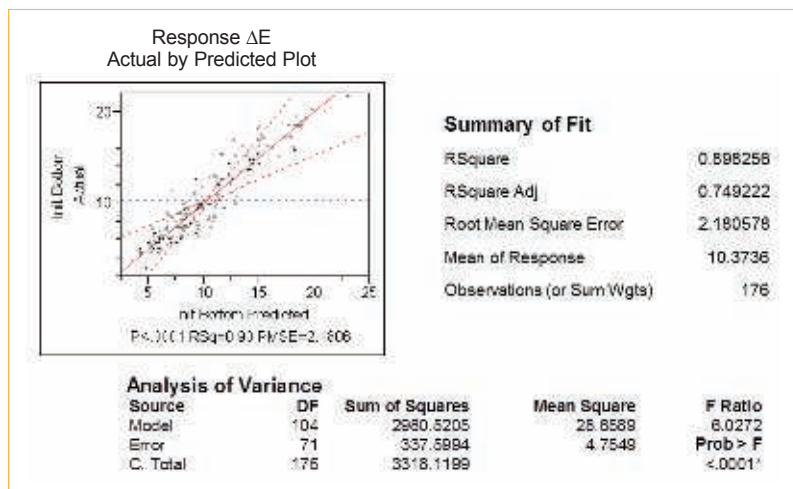


Figure 11—Model of ΔE vs. additives.

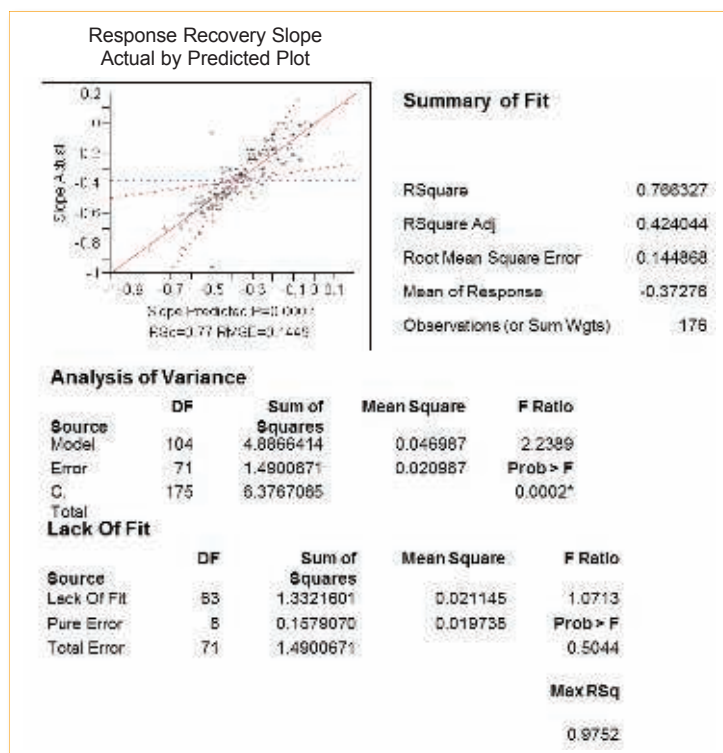


Figure 12—Analysis of recovery.

Measurement of Color to Evaluate Defoamer Effectiveness

Through visual examination of the images taken, it was thought that it might be possible to correlate the color change, ΔE , with the amount of entrained air in the liquid phase. As can be seen in *Figure 9*, the color of the liquid solution appears to change with the amount and size of entrained air in the liquid phase.

The proprietary software program used to measure color allows the user to define the area of space on an image to be measured for color, as shown in *Figure 10*. The ΔE values are then calculated for each sample using the initial image and the image taken one minute after the shaking step. Using JMP (SAS Institute) statistical software, a model is fit using additive class, additive name, and the amount of additive (including second order interactions) to produce a statistically significant model, as shown in *Figure 11*.

Additionally, a recovery rate can be calculated for each sample by graphically plotting ΔE versus time. Assuming a linear rate of recovery, the resultant recovery slope of each sample can then be fit into a statistical model as shown in *Figure 12*. It is expected that a more in-depth analysis of the recovery rate, i.e., nonlinear solutions, would significantly improve this model.

In some instances, the shaken formulations segregate into two distinct phases over time, as shown in *Figure 13*. If the user only measures the color in the lower section of the images, the data would suggest that this formulation has recovered to its original state. The proprietary software has the advantage of allowing the user to select multiple locations on each image upon which to record color values. This allows for color data to be measured in both the lower and upper sections of the images of the PPR vials, as represented by the boxes in *Figure 13*. The upper and lower color values can then be used, either as an additive or a weighted value, to better evaluate the true recovery of each formulation.

Reproducibility of the Control

During this experiment, 16 controls, without additives, were placed at random in the 96 well plates. The measured values are shown in *Figure 14*. The distributions are fairly well behaved for both the measured ΔE values and the recovery slope, indicating good reproducibility of the method.

CONCLUSION

The novel high throughput method presented here allows for surfactants to be screened by



Figure 13—Analyzing phase separation.

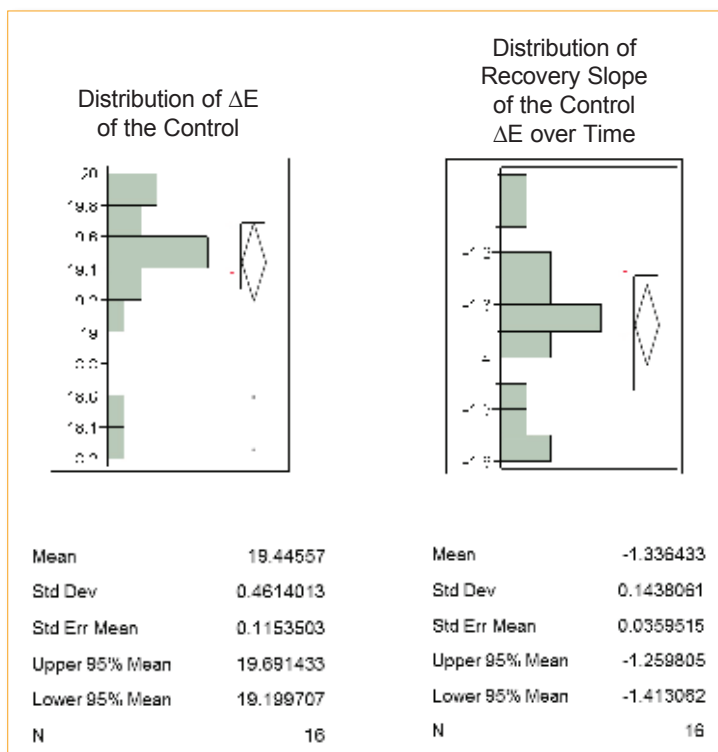


Figure 14—Analysis of the control.

evaluating their effect on air entrainment and stabilization in a clear coating formulation. Based on this analysis, surfactants can be selected and further evaluated via conventional benchtop methodologies. This differentiated method also allows for the possibility of using “shear rate” as a variable by manipulating the type and amount of beads used, as well as the speed and test time of the wrist shaker. In the future, it may be possible to model and control this complicated mixing environment, to realistically simulate manufacturing or application conditions. Extended analysis can also be performed by evaluating the rate at which a liquid formulation can recover to its original state over an extended time scale. Furthermore, the unique approach of using the color of the liquid coating as a comparative tool to evaluate

the relative amount of air in the liquid coating has been shown to be both accurate and reproducible.

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