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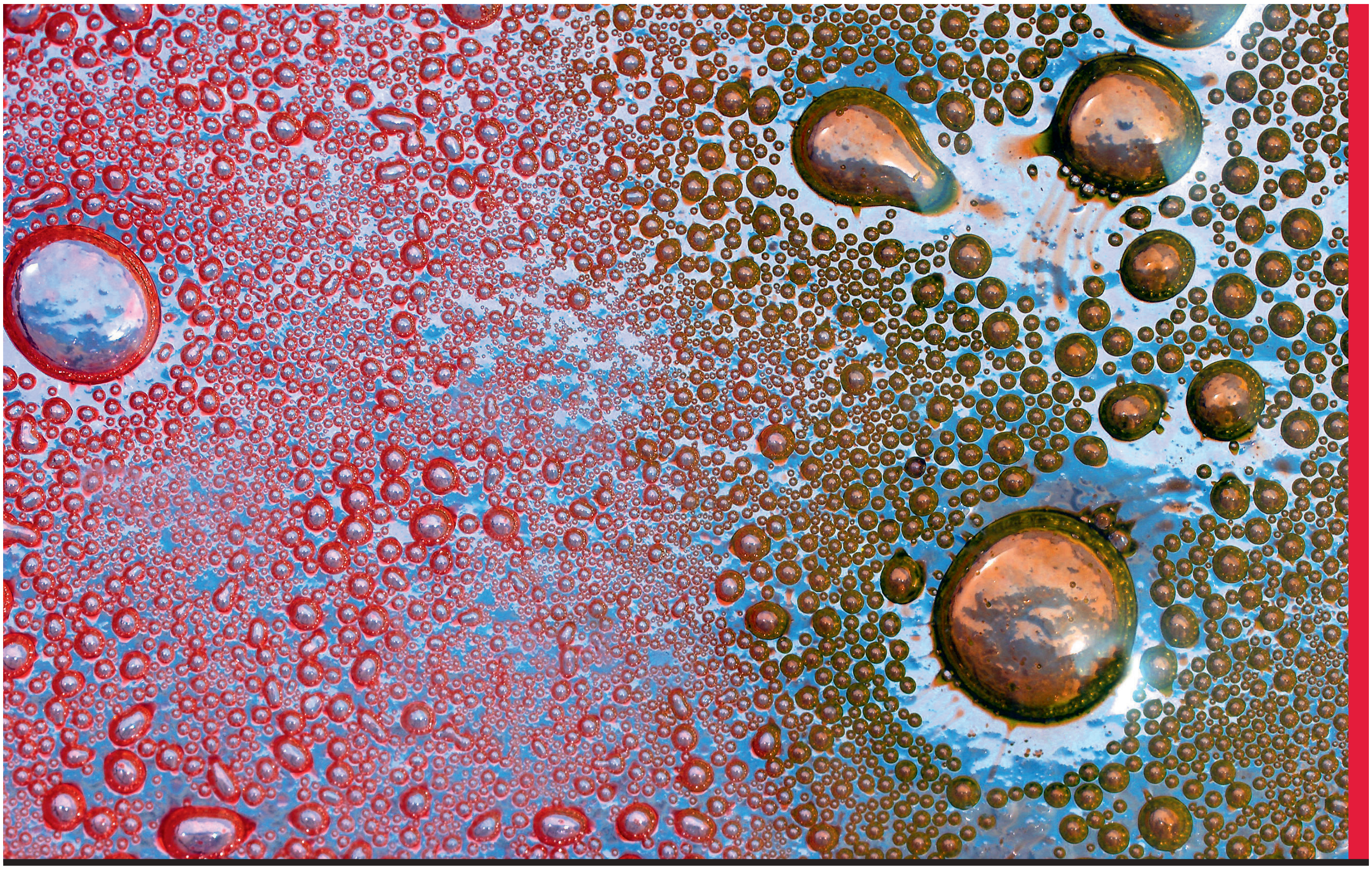


CAUGHT ON CAMERA

Defoamer performance measured by evaluation of coating film appearance. By Mojgan Nejad, Maryam Arefmanesh, Katie Henderson, Javad Esmaeelpanah, Sanjeev Chandra, and Javad Mostaghimi

To prevent air entrapment and foaming, defoamers are usually added to water-borne coating formulations. Defoamer performance was studied by capturing high resolution images of a coating sprayed on glass substrates. Image analysis provided a quantitative measure of the efficacy of additives. Surprisingly, the most effective product was a non-ionic wetting agent rather than a defoamer.

In addition to decorative purposes, coatings are applied on wood surfaces to improve their performance [1]. Of the various coating formulations, polyurethanes (PU) have the highest abrasion and chemical resistance [2]. Until recently, PU solvent-based coatings were dominant in the wood coating market. However, due to environmental legislations and consumer preference, the market is shifting to water-based formulations [1].

One of the main challenges in this technology shift is how to reduce the surface tension of water-based coatings closer to the surface tension of solvent-based coatings, which is around 25 mN/m [3]. In order to have good wetting and adhesion, the surface tension of any formulated coating should be significantly lower than the surface energy of the substrate it is to be applied to [4].

For instance the surface energy of wood is around 44 mN/m [5] while water has a surface tension of 72 mN/m; therefore, different additives are used in water-based coating formulations to reduce the surface tension towards that of the coating itself, which is around 30 mN/m [3].

During drying, if the surface viscosity of the applied film becomes too high the bubbles formed cannot escape from the surface and will become entrapped in the coating film. In addition, the formation of CO_2 due to the reaction of isocyanate with water can also cause bubble formation problems in water-based polyurethane coatings [2, 6].

Defoamer additives are used to prevent air entrapment and foaming. Defoamers are low surface tension liquids that can enter the foam lamella [7], or act as a carrier medium to transport hydrophobic particles into the foam lamella; both will cause the foam lamella to collapse [7]. Block-copolymer defoamers are commonly used in new water-borne formulations [8]. Although it is relatively simple to predict which type of additives will break down the bubble lamella, detailed predictions are very difficult because there are a variety of components that could potentially end up at the foam interface [6].

To deal with foaming of a new coating formulation, it is critical to look at the combination of surfactants, wetting agents, water-soluble polymers and antifoams [6]. The main objective of the current study was to design an accurate quantitative study that measures the effects of different additives on bubble formation and dissipation in water-borne polyurethane resin formulations.

SURFACE TENSION MEASUREMENT PROCEDURE

A two-component water-based aliphatic polyurethane resin (from Daotan) designed for formulation of clear topcoat wood coating was used as the base resin in this study. A number of commercially available defoamers and general additives usually recommended for wood coating formulations were also obtained from different manufacturers. The surface tension of pure resin was measured and compared to that of resin after being mixed with various additives at different concentrations. These measurements were performed using a "Sigma 70" tensiometer with the Wilhelmy plate (22 x 50 x 0.15 mm) method with an average of ten readings for each sample.
In all bubble studies, the additives were mixed with the resin following the exact ratio as recommended by the manufacturer for the formulation of the wood coating. Experimental analysis was conducted to quantitatively and qualitatively determine the effects of different additives used in the coating formulation on bubble count, bubble size and their changes in the 15 minutes immediately after spraying. For this study, the effects of each additive were tested individually. Each formulation thus contained two components: pure resin and one of the additives of interest. The names of all additives and the concentrations used in the study are shown in the first two columns of *Table 1*. These combinations were completely mixed using a wooden stirrer and then sprayed on the glass using a hand-held compressed air spray gun.

APPLICATION AND IMAGING PROCEDURE

The number of spray passes was adjusted based on the density of resin and surface area of glass so that that the final film would have a wet film thickness of around 150 µm. The glass substrates used were heat-resistant borosilicate squares (5 x 5 x 0.3 cm by McMaster-Carr). Once the spraying was complete, the coated-glass substrates were placed under the digital SLR camera (Nikon "D90") for imaging, as can be seen in *Figure 1* (left).
In order to better control the accuracy of still-shot timing, a timer system (TC-N3, JYC Technology) was used. An LED light panel (from Porta-Trace) with work surface dimensions of 22 cm by 27 cm and a bright white LED was used as the light source. A light box was also placed around the setting to shield the camera from external light sources.
An image of the complete experimental set up can be seen in *Figure 1* (right). Images were taken every 5 seconds for 15 minutes. The images were then processed using "ImageJ" software, utilising a macro that provided a summary including bubble count and average bubble size for each image analysed.

RESULTS AT A GLANCE

→ The low evaporation rate and high surface tension of water makes water-based formulations prone to bubble entrapment and blistering defects. Air bubbles can form during manufacturing, packaging and application. To prevent foam problems, defoamers are usually added.

→ The effects of different additives on bubble formation and dissipation were studied by capturing high resolution images of a water-based polyurethane resin coating sprayed on glass substrate.

→ Image analysis shows that certain additives reduce the number of both bubbles formed initially and the number that remain after 15 minutes in the wet film. The quantitative analysis gives accurate comparisons of the efficacy of the defoamers tested.

→ The addition of a non-ionic wetting agent resulted in almost no bubble formation, which was surprisingly better than all the defoamers evaluated in the study.

Figure 1: The camera set-up (left) and the experimental set-up for bubble measurement study (right)

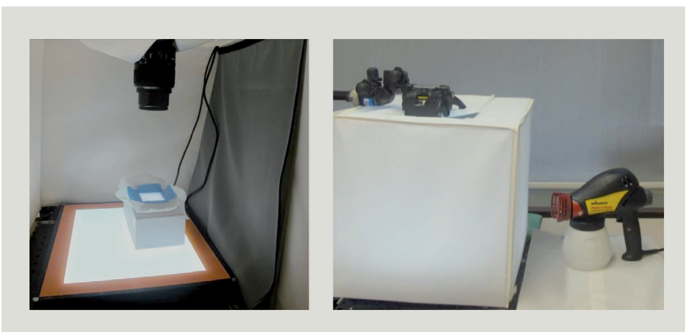


Figure 2: Pure PUD resin images after processing (area under observation is 33 x 21 mm)

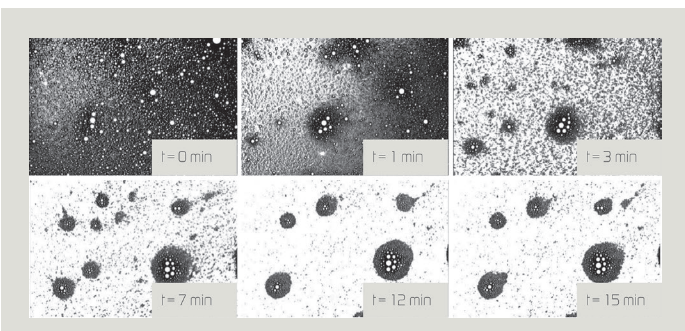
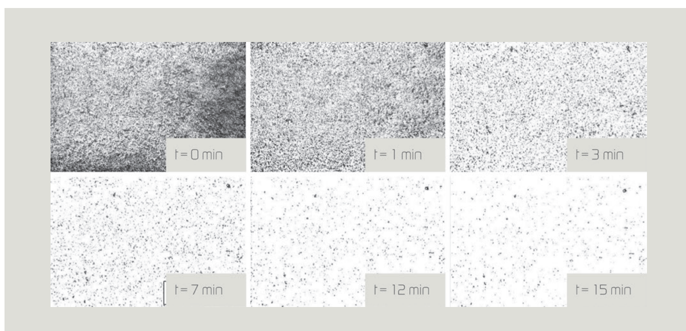


Figure 3: Byk-346 (0.35 wt%) surfactant + resin images after processing (area under observation is 33 x 21 mm)



IMPACT OF VARYING ADDITION RATES IS CHECKED

The results of the surface tension measurements are summarised in *Table 1*. Measurements were taken for each additive at a fixed concentration of 0.1 % and then compared to that of the surface tension resulting from the concentrations currently recommended for the formulation of the wood coatings.

Two factors should be considered when determining the benefits of an additive with respect to surface tension: the magnitude of the decrease in surface tension between the pure resin and the additive/resin formulation, and the difference in surface tension when comparing the two concentrations studied.

In addition to this, the data provides an indication of the concentration needed to reduce the surface tension. If the surface tension of a 0.1% formulation is similar to that of a higher concentration, that means there is no need to use a higher amount.

For instance, the micro-defoamer ("Surfynol MD 20") had an even lower surface tension when only 0.1% was added. That means not only is a higher concentration unnecessary, but a higher amount even gives slightly negative effects on surface tension.

Another example is "Byk-346" surfactant, which is a polyether-modified polysiloxane additive recommended for the reduction of surface tension. The addition of 0.1% to the resin reduced the surface tension to 25.8 mN/m which is very close to the surface tension result after the addition of 0.3% (25.0 mN/m). The higher addition is therefore of little benefit.

RESULTS OF BUBBLE ENTRAPMENT STUDY

Initial and final bubble count and size varied for different additives. In each case, the bubble count decreased with time until a final bubble count was reached during the 15 minute image analysis study. *Figures 2-6* show snapshots of processed images taken at t = 0, 1, 3, 7, 12 and 15 minutes for different additives. The resolution of each image was 4288 x 2848 pixels. *Table 2* shows a summary including initial and final bubble count and bubble size for each additive tested.

The pure resin started with the complete surface covered with bubbles in different sizes. The bubbles then started moving around, colliding with each other and coalescing to form a few large bubbles, an effect due to the surface tension gradient created around the bubbles (*Figure 2*). Gradually some of those bubbles popped, reducing the number on the surface, but still many of the bubbles remained on the surface even after complete air-drying of the resin (after 24 hours).

The addition of a silicone-based surfactant ("Byk-346") eliminated the formation of large bubbles, yet the initial number of small bubbles was high and some still remained after 15 minutes of observation time (*Figure 3*).

Figures 4 and *5* show images taken from the addition of two defoamers produced by the same company. The new formulation called "Foamex

Figure 4: Foamex 800 (0.39 wt%) + resin images after processing (area under observation is 33 x 21 mm)

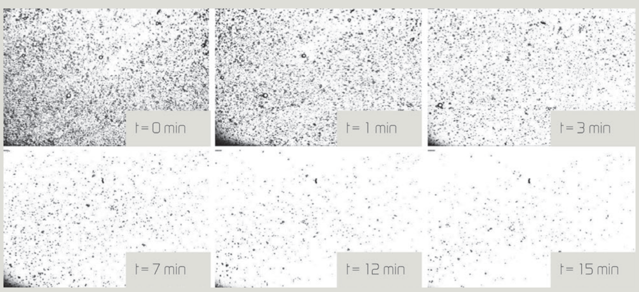


Figure 5: "Foamex 822" (0.39 wt%) + Resin images after processing (area under observation is 33 x 21 mm)

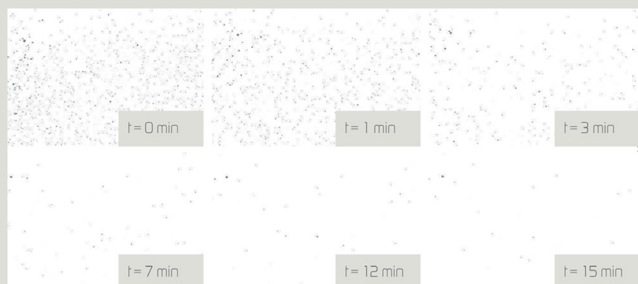
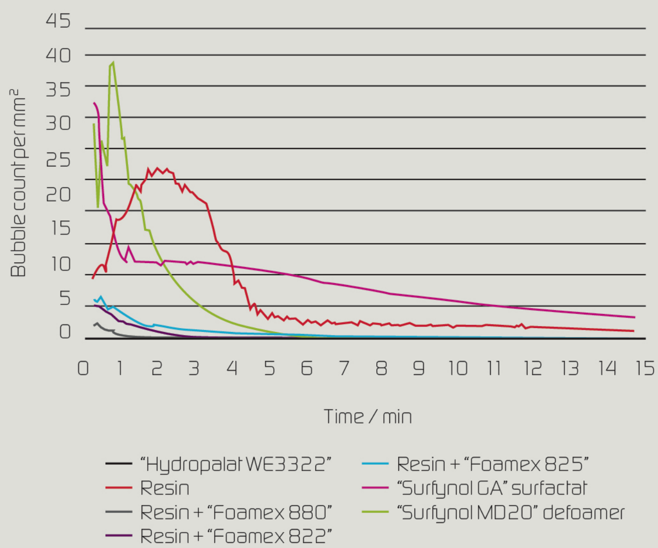


Figure 6: "Hydropalat WE3322" (0.95 wt%) + resin images after processing (area under observation is 33 x 21 mm)

Figure 7: Bubble count per mm² vs. time for pure resin and mixture of some additives with resin



822" is clearly much more effective than "Foamex 800". The first is indeed recommended as a more effective formulation than the latter by the producer.

As can be seen from *Figure 6*, the non-ionic surfactant used as a wetting agent ("Hydropalat") was the most effective additive in reducing the initial foam formation in the resin, also resulting in fast dissipation of the few small bubbles formed.

Trends showing the reduction in bubble count over give an indication of the potential benefits of each additive. *Figure 7* shows in detail the bubble count of a number of additives and resin over time. In some cases like the pure resin as shown in *Figure 7*, there is an increase in the number of bubbles in the first few minutes which could be explained by movement of dissolved bubbles in the film to the surface and then a gradual decrease in number of bubbles is seen as they escape from the surface.

PROCEDURE OFFERS POTENTIAL FOR MORE DETAILED STUDIES

The unique design of this study allowed accurate comparisons of the efficacy of a number of defoamers, surfactants and wetting agents in foam reduction when added to a water-based poly-urethane resin formulation. Detailed studies showing the number of initial bubble formations and their dissipation with time will help producers of defoamers to have a better view of existing issues.

These results along with surface tension analysis will also help the paint formulator to choose the best possible defoamer and know the exact amount needed for formulation. Among all additives tested in this study, a non-ionic surfactant showed the most promising results with the lowest initial bubble formation and an almost completely bubble-free wet film after 15 minutes observation time.

More in-depth study in close collaboration with the paint raw material producer is needed to explain these observation effects, based on the chemistry of surfactants or defoamers and how it can be utilised for a wide range of resin types and formulations.

Understanding the mechanisms which reduce the formation of bubbles and their faster dissipation in the liquid film of water-borne coatings will be a breakthrough study for major producers of coatings additives and coating industries. More work is needed to confirm the effect of the combination of additives and the optimal order of their addition in the bubble entrapment study.

Bubble movement in paint during drying or curing time and the mechanisms that would either hold them to the substrate or push them to the surface to pop is the emphasis of ongoing research at the Centre for Advanced Coating Technologies at the University of Toronto.

Table 2: Surface tension of pure resin and mixtures with additive at recommended rate to wood coating formulation and also at 0.1% for uniform comparison

Raw materials	% additives as recommended	Surface tension (mN/m) 0.1 %	Surface tension (mN/m) % as recommended
Pure resin (Daotan)	83	44.7	44.7
"Foamex 800" (Defoamer)	0.4	37.1	31.8
"Foamex 822" (Defoamer)	0.4	35.2	32.5
"Foamex 825" (Defoamer)	0.4	31.5	30.7
"Airex 902 W" (Defoamer)	0.4	38.8	37.5
"Surfynol MD 20" (Micro defoamer)	0.2	28.7	29.3
"Hydropalat WE 3322" (Wetting agent)	0.9	28.9	28.7
"Rheovis" (Thickener)	0.1	39.9	39.9
"BYK-346" (Surfactant, silicone)	0.3	25.8	25
"Surfynol GA" (Surfactant, non-ionic)	0.3	41.5	40.3
"Michem" (PE wax emulsion)	4	44.8	22.5
"Twin 4100" (Surfactant)	0.9	20.9	21.2
"EnviroGem" (Surfactant)	0.3	30.7	30.7
"Dynol 960"(Superwetting siloxane surfactant)	0.3	23.8	23.9
"Acematt" (Matting agent)	0.8	45.3	46.9

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Table 3: Initial and final bubble counts and bubble size of pure resin and mixture of resin with each additive

Additive	Initial bubble count (per mm²)	Final bubble count (per mm²)	Initial average bubble size (mm²)	Final averagebubble size (mm²)
Pure resin	19.6	1.19	0.04	0.11
"Acematt"	61.7	18.7	0.05	0.08
"BYK-346"	50.0	0.82	0.06	0.08
"Foamex 800"	48.8	0.66	0.05	0.07
"Foamex 822"	6.21	0.04	0.04	0.07
"Foamex 825"	6.91	0.23	0.04	0.08
"Surfynol MD20"	34.4	0.09	0.03	0.07
"Hydropalat WE3322"	0.41	0.09	0.03	0.06
"Michem" Emulsion	35.1	3.83	0.06	0.08
"Rheovis"	21.0	4.31	0.05	0.10
"Surfynol GA"	37.9	2.90	0.05	0.09

"Addition of a very small amount of the non-ionic wetting agent significantly reduced the surface tension of the resin."

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Three questions to Mojgan Nejad

How do you explain the good performance of the non-ionic wetting agent? *The nonionic wetting agent ("Hydropalat WE3322") which was used in this study in addition to its wetting properties had a defoaming capability by destabilising foams. The good performance of this additive might be partially explained by the fact that the addition of a very small amount (0.1%) resulted in a significant reduction of the resin's surface tension (from 44.7 mN/m to 28.9 mN/m). However, further in-depth study is needed to look at the chemistry of the resin and defoamers in order to explain the exact mechanism by which this additive performs in comparison with other additives*

To what extent is bubble formation tolerable in water-borne coatings? *The amount and also the average size of the bubbles that can be tolerated in any formulation depend on the final application of the coatings. For instance, if the formulation is designed for high-end custom-designed wooden cabinets, then having even a small number of bubbles, which are usually trapped at the corners or edges of the cabinet doors, will negatively affect the gloss and the general appearance of the products. Thus, for these applications, the coating has almost zero tolerance for bubbles. While, for other applications like exterior decks, fences and sidings to have some small entrapped bubbles would not create any visible defect on the coating's appearance.*

Can bubble formation only be avoided by using an additive? *It depends on the size, number of bubbles and the stage that they form. Some resin formulations might have fewer bubbles to start with which may pop-up before drying of the film and would require no additives for adjusting the formulations. Additionally, it may depend on the stage that bubbles form for instance during application (spray or brush), in spray coatings droplet size and velocity play an important role in bubble entrapment. Bubbles are created when droplets approach a substrate and the air pressure in the gap separating the two increases, creating a depression in the droplet surface in which air is entrapped. Reducing droplet diameter and impact velocity both diminish the likelihood of air bubbles being formed, solving the issue without the use of additives.*