

# Development of Low VOC Additives to Extend the Wet Edge and Open Time of Aqueous Coatings

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One of the challenges of formulating waterborne coatings is achieving an acceptable balance of properties both during the film application and drying process as well as in the final film. This difficulty is compounded by regulations relating to the reduction of volatile organic compounds (VOCs) in architectural coatings. There is a competition between the requirements for adequate workability time of the coating with appropriate film formation and recoat behavior. The period in which irregularities in a freshly applied coating can be repaired without resulting in brush marks is referred to as the *open time*, while the period in which a coating can be applied over an existing paint film without leaving lap marks is deemed the *wet edge time*. Aqueous coatings generally employ dispersed high molecular weight polymers as binders. These binders often provide short open times when the coating is dried since the dispersed polymer particles tend to be immobilized quickly in the edge region of an applied coating. As a result, the viscosity of the coating increases rapidly, which leads to a limited window of workability. Small molecule alkylene glycols such as ethylene and propylene glycol are routinely incorporated in aqueous coatings as humectants, but are limited in utility since they are considered to be VOCs. This paper describes the process by which new, low VOC additives were developed to improve open time and wet edge in aqueous coatings. Mechanisms for the enhanced performance will be outlined through use of novel rheological techniques. Paint performance properties will be exemplified in a typical architectural formulation.

## Background

While a significant amount of literature has been published on the processes related to film formation and coalescence, there has been less focus on fundamental mechanisms related to the impact of glycols and other additives on the workability of waterborne architectural paints. In 1974, Andrews<sup>1</sup> studied the influence that ethylene and propylene glycol impart on the drying behavior of latex paints. He noted that although ethylene glycol is more hydrophilic than propylene glycol, it evaporates more slowly from formulated coatings. Examination of weight loss and compositional information for systems applied under a range of temperatures and relative humidities revealed that propylene glycol begins to evaporate as soon as the paint is drawn down at elevated temperature, but does not leave until about half of the original volatiles have evaporated at lower temperature. Sullivan<sup>2</sup> assessed the influence of organic solvents with a variety of partition coefficients on evaporation rates in latex paints. He concluded that more hydrophilic solvents, such as ethylene glycol, tend to partition predominantly into the aqueous phase, which allows them to diffuse out of the coating more readily than a hydrophobic coalescent, which largely partitions to the polymer. Interestingly, it was noted that ethylene glycol accelerates coalescent evaporation, and it was proposed that the glycol creates a pathway in the hydrophilic network through which the coalescent may more easily escape. Croll<sup>3</sup> studied the drying of latex coatings, and confirmed Andrews' finding that the weight loss of ethylene glycol appears to occur after the majority of the water has evaporated. Croll proposed a two stage drying process in which water evaporates from the edges and

surface of a drying coating at a constant rate followed by a stage in which evaporation is restricted due to changes in the wet interior of the coating. It is noted that short open times in latex paints could be linked to both the speed at which water evaporates from a coating as well as the dry layer forming on the exterior of the film. Winnick<sup>4</sup> compared the dry time of latexes with high and low glass transition temperatures ( $T_g$ ) as compared to a blend of latexes, and found that hard (high  $T_g$ ) latexes dry more rapidly than soft (low  $T_g$ ) latexes, while some blends of the two dry more slowly than either of the individual latexes. Hard latexes do not deform during drying, which leaves a pore structure through which water can pass. In blended systems, softer latexes can deform and fill the voids between harder particles, which hinders evaporation. It was proposed that drying proceeds inward from the edge and a 'drying front' exists at the boundary between the dried film and the wet dispersion such that water is driven to this front where evaporation can occur more readily than from the surface of the drying film as illustrated in Figure 1. The rate of propagation of this drying front may relate to open time in latex paint systems.

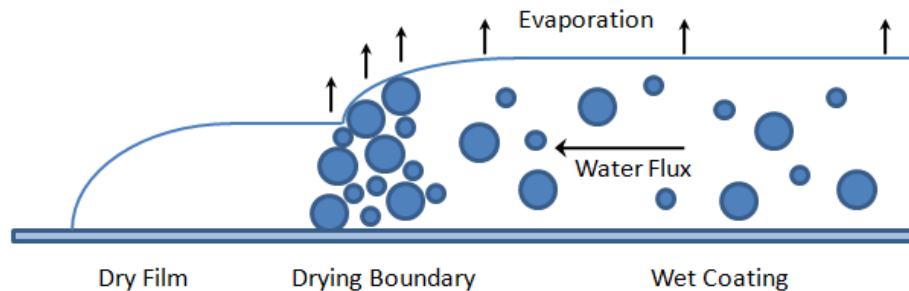


Figure 1. Idealized mechanistic view of the drying process, adapted from Winnick<sup>4</sup>

Salamanca<sup>5</sup> examined the lateral drying in waterborne latexes using magnetic resonance microscopy and determined that open time increased substantially above a particular reduced capillary pressure  $p_{cap}$ , in agreement with a model published in 1998 by Routh<sup>6</sup>. Equation 1 (from Salamanca<sup>5</sup> and Routh<sup>6</sup>) suggests that open time should increase at elevated  $p_{cap}$ , since the recession of the water front is slower.

$$p_{cap} = \frac{20}{75} \left( \frac{3\gamma\eta_0}{E} \right)^{1/2} \frac{a(1 - \phi_m)}{\mu\phi_m^2 H} \quad (1)$$

In the above equation,  $\gamma$  is the surface energy of the liquid,  $\eta_0$  is the zero shear viscosity for the latex,  $E$  is the evaporation rate,  $a$  is the radius of the particles,  $\phi_m$  is the volume fraction solids at close packing,  $\mu$  is the viscosity of the continuous phase, and  $H$  is the initial film thickness. Salamanca<sup>5</sup> studied the influence of  $p_{cap}$  on open time by varying particle radius, evaporation rate, and film thickness which led to  $p_{cap}$  values ranging from 1 to 417. It was observed that at low  $p_{cap}$ , water recedes from the sample edge immediately, while at high  $p_{cap}$ , the water is 'pinned' at the edge for about half of the drying time<sup>5</sup>. As a result, open times were found to be relatively short for  $p_{cap}$  values below 15 while open times were substantially longer at higher values of  $p_{cap}$ .

Numerous techniques to characterize open time, wet edge, and viscosity build during cure have been described in recent publications. One of the most common techniques for evaluation of open time and wet edge requires a paint film to be drawn down on a sealed chart using a 3 mil Bird bar. A series of 'X'

marks are made in the center of the drawdown in accordance with Figure 2. After fixed periods of time, paint is brushed four cycles back and forth across the film. The point at which the edge of the drawdown can no longer be worked into the body of the paint is referred to as the wet edge time, while the time at which the 'X' begins to show through the paint is deemed the open time<sup>7,8</sup>. A similar test method is under development by ASTM.

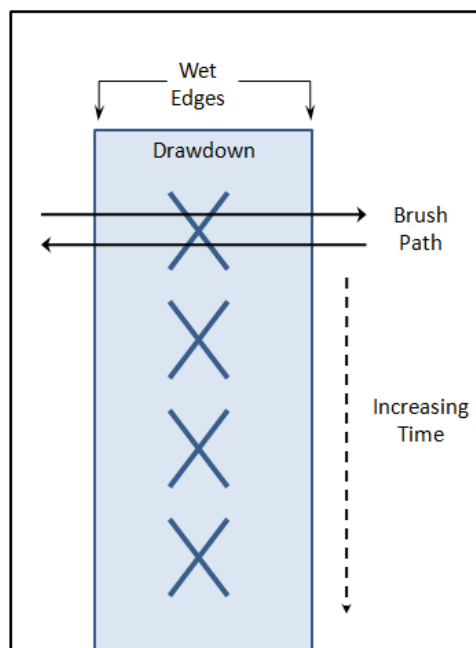


Figure 2. Typical test method for open time and wet edge testing

Monaghan described a brushed flow out test as a method to assess brush marks as a measure of paint flow out during drying<sup>7</sup>. Akkerman<sup>8</sup> and Browning<sup>9</sup> utilized a technique termed 'Falling Wave Analysis' by which a sinusoidal applicator is utilized to create unevenness in a wet film on a substrate that can be controlled in terms of temperature and angle of tilt during dry. Changes in amplitude are related to leveling, while wave shifts provide information on sagging, and loss of fluidity may be related to open time. Rheological measurements also provide unique insight on viscosity development in drying films. Molenaar<sup>10</sup> outlines the applicability of a 'filmviscometer' where the velocity with which a steel ball rolls through a drying coating held at an angle may be related to an apparent viscosity. By measuring the velocity with time, the apparent viscosity can be determined as a function of drying time, which may be related to sag, leveling, and open time. Löfflath<sup>11</sup> compared open time from a modified dry time recorder with that calculated from the point of infinite viscosity as measured by creep mode rheology using a cone and plate viscometer on coating samples collected after being dried for different times. Results indicated good correlation between open time from the rheometer and dry time recorder.

### Impact of VOC Regulations

Over the past decade, there have been significant changes in the regulations governing the use of volatile organic compounds (VOCs) in architectural coatings. In the United States, several regulatory bodies have

VOC restrictions, including SCAQMD (South Coast Air Quality Management District), OTC (Ozone Transport Commission), CARB (California Air Resources Board), and the US Environmental Protection Agency (EPA). The usage of VOCs has been, and will continue to be curtailed by these new regulations. The European Union (EU) is covered by the Decopaint Directive 2004/42/CE of the European Parliament, which was issued on April 24, 2004. Annex II of this directive outlines two sets of VOC limits for paints and varnishes, one that was implemented on 1/1/2007, and a more stringent standard came into force as of 1/1/2010. The two major sources of VOC in architectural coatings are the open time / freeze-thaw additives and some coalescents. Although the definitions for VOC differ from region to region, small molecule alkylene glycols used to improve open time and wet edge are universally considered to be VOCs. Implementation of these more restrictive regulations has led to significant research aimed at determining the most effective approaches to maintain the application and performance properties of coatings at reduced VOC.

Open time and wet edge are often compromised when ethylene or propylene glycol are removed from a formulation. There has been significant innovation over the last few years focused on improving workability of low VOC architectural paints either through new additives or by novel binders. It is well recognized that low VOC paints are less robust to application across broad shifts in environmental conditions. A solution is desired that will improve open time / wet edge time and maintain the recoat window without negatively impacting film properties such as scrub resistance and wet adhesion or contributing substantially to VOC.

### **Additive Development and Evaluation**

The goal of this work was to design an additive that would serve as a low VOC, low emission approach to improve the wet edge and open time of latex paints without compromising paint performance. The target was to provide performance observed in 150 g/L paints (US) at a reduced VOC of 50 g/L. Both ethylene and propylene glycol are considered to be humectants, which are hygroscopic materials that are used to promote the retention of moisture. Based on this definition, it may be stated that materials that slow the evaporation rate of water could serve to improve workability in latex paints. Ethylene glycol has a boiling point of 196°C, while propylene glycol boils at 187°C. In order to develop lower VOC materials that bring similar function, it is necessary to increase molecular weight in order to decrease volatility. The problem with this approach is that higher molecular weight, higher boiling additives are more likely to be retained in a dried paint film, which can lead to issues with water resistance and wet adhesion due to their highly hydrophilic nature and issues with block resistance due to their persistence in coatings.

Initially, a series of potential materials was screened for efficacy with respect to open time and wet edge improvement by post-adding candidate additives to a commercial semigloss paint. These paints were then evaluated for a limited set of properties, including open time as previously outlined in Figure 2. From this work, a subset of promising, low VOC materials that could be further tailored was identified. Subsequent work was carried out in formulated paints to avoid complexities associated with post-adding to commercial controls. An acrylic semigloss formulation was chosen as the basis for the work. The formulation is outlined in Table I.

Table I. Control formulation used as a basis for additive development

| Ingredient           | Pounds  | Gallons | Properties                    |
|----------------------|---------|---------|-------------------------------|
| Ti-Pure R-746 slurry | 324.63  | 16.73   | PVC, %: 20.6                  |
| Water                | 138.13  | 16.58   | NVV, %: 28.2                  |
| Kathon LX1.5%        | 1.89    | 0.22    | <b>VOC</b>                    |
| Rhoplex SG-30        | 505.79  | 57.48   | 130 g/L (US, less water)      |
| Texanol              | 11.52   | 1.46    | 39 g/L (Europe, ready to use) |
| Aerosol OT-75        | 1.57    | 0.17    |                               |
| BYK-022              | 2.09    | 0.25    |                               |
| Propylene Glycol     | 31.42   | 3.65    |                               |
| Acrysol SCT-275      | 4.92    | 0.57    |                               |
| Acrysol RM-2020NPR   | 25.24   | 2.89    |                               |
| <b>Total</b>         | 1047.19 | 100.00  |                               |

A series of designed experiments was carried out in which the candidate additives were substituted in place of the propylene glycol. Additives that contained water were substituted such that 3% actives were incorporated, and an equivalent amount of water was removed from the formulation to keep total water content on target. Properties that were evaluated included open time, wet edge time, scrub resistance, block resistance, gloss, and wet adhesion. A range of materials was identified that could substantially increase open time at reduced VOC, but it was clear that improving workability while balancing other paint properties was a more significant challenge. The designed experiments identified a candidate that could be tailored by adjusting several parameters to yield a balance of properties. The influence of each parameter is illustrated in Figure 3.

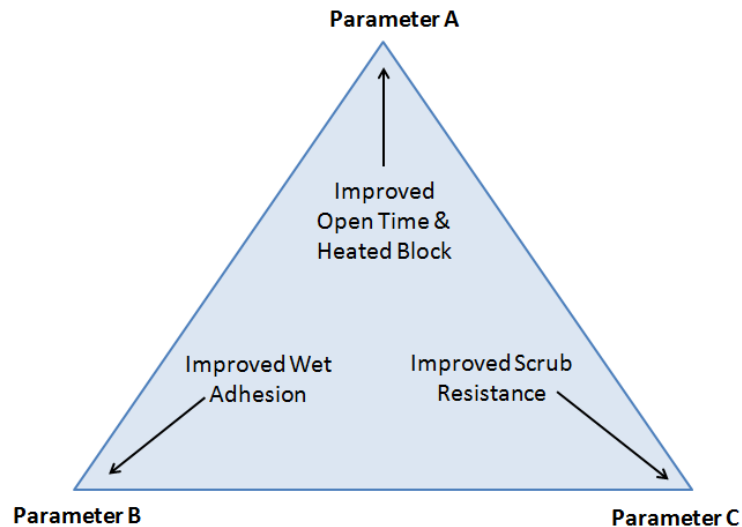
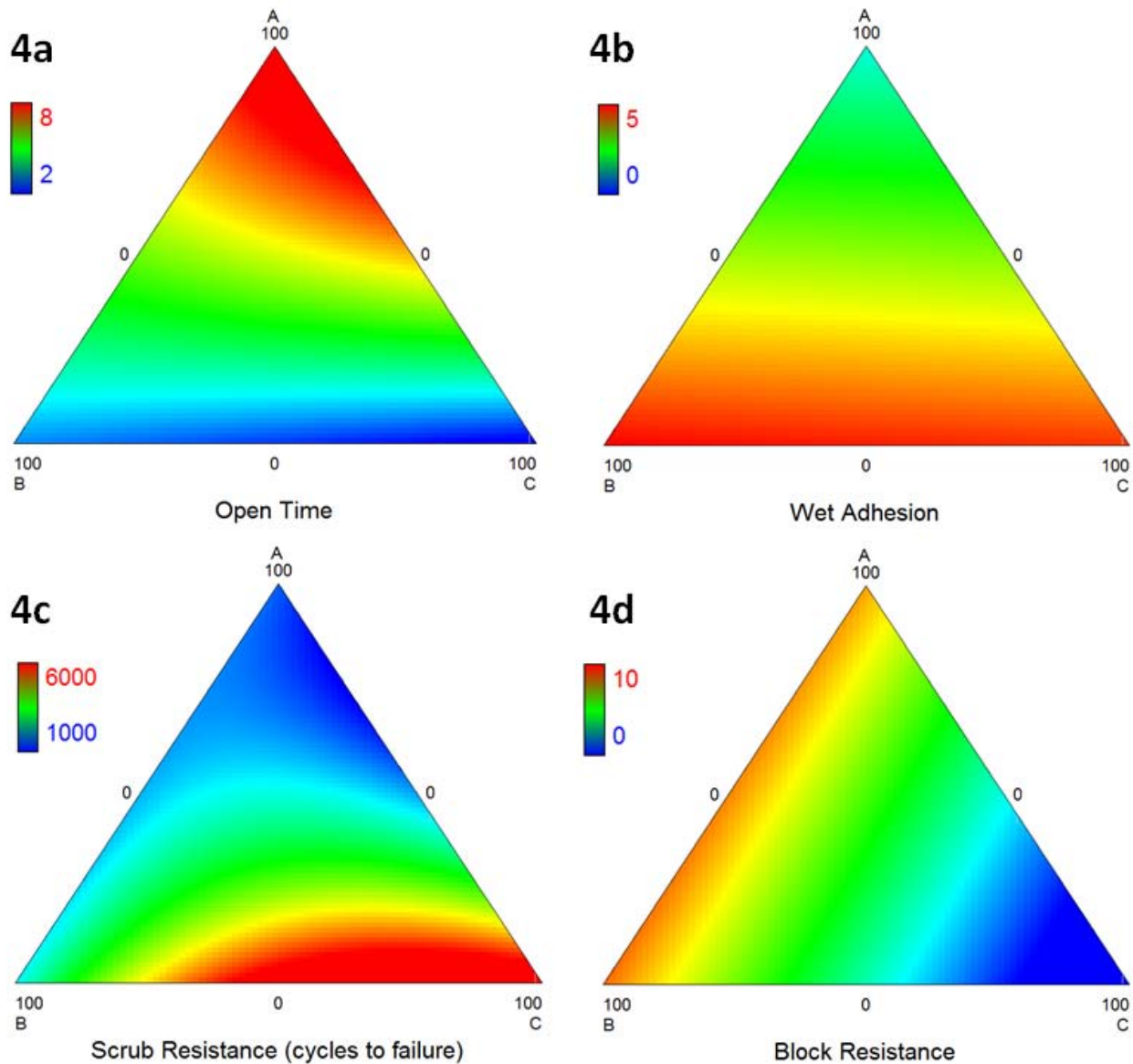


Figure 3. Impact of additive design parameters on balance of properties in formulated paint

Results of the designed experiment are outlined in Figure 4a – 4d. Figure 4a illustrates that parameter A has the strongest influence on improving open time. This design space provided open times ranging from about 2 to 8 minutes, as compared to the higher VOC control which had an open time of 5 minutes. Figure

4b provides an analogous assessment of wet adhesion (ASTM D6900), which is most positively impacted by parameter B, and is maximized in the lower left hand corner of the design space. The wet adhesion rating of the control was about 4.5. Figure 4c provides the scrub resistance (ASTM D2486) values. For this property, parameter C has the greatest influence and scrub is much higher than that of the control in the lower right corner of the design space. Figure 4d illustrates that heated block (ASTM D4946) is most significantly influenced by parameter C, and is maximized when parameter C is minimized. The control had a heated block resistance of 7.



Figures 4 a-d. Results of experimental design in which parameters A, B, and C were varied, and response in terms of open time, in minutes (a), wet adhesion (b), scrub as percent of control (c), and heated block (d)

From this data, it is clear that it may not be preferable to maximize open time since scrub resistance and wet adhesion may then be unacceptable. Instead, an optimization can be carried out on this data in order to establish how an additive should be tailored to provide a good balance of properties at reduced VOC. From this work, composition was determined for a developmental open time additive (OTA). The selected OTA is a liquid with a viscosity of about 8500 cP, about 70% active material, less than 1% VOC (Europe), and a density of 1.08 g/cm<sup>3</sup>. Table II provides a summary of the paint evaluations comparing the control paint from Table I to a paint formulated with OTA at 3% actives. The data from Table II indicates that the OTA provides a reasonable balance of properties as compared to the higher VOC control formulation.

Table II. Summary of performance properties of control paint vs. paint formulated with OTA

|                                 | Control Paint (3% PG) | Paint (3% OTA actives) |
|---------------------------------|-----------------------|------------------------|
| VOC (US)                        | 130 g/L               | 40 g/L                 |
| VOC (Europe), ready to use      | 39 g/L                | 3 g/L                  |
| Open time                       | 5 minutes             | 7 minutes              |
| Wet edge                        | 2 minutes             | 4 minutes              |
| Gloss, 20° / 60°                | 40 / 71               | 58 / 84                |
| Scrub resistance (% of control) | 100                   | 101                    |
| Block resistance                | 7                     | 6                      |
| Wet adhesion                    | 5                     | 4                      |
| Stormer viscosity               | 96                    | 96                     |
| ICI viscosity                   | 1.1                   | 1.0                    |

One of the challenges for the application of waterborne architectural paints is the variation in the workability that is observed over different environmental conditions. Figure 5 illustrates the change in drying speed for the control paint at three relative humidities measured on a TA Instruments Q5000 SA.

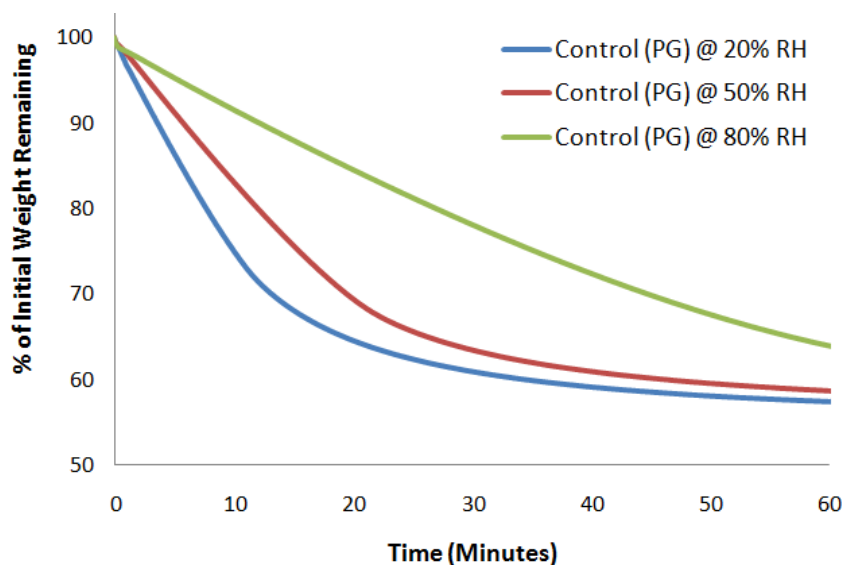
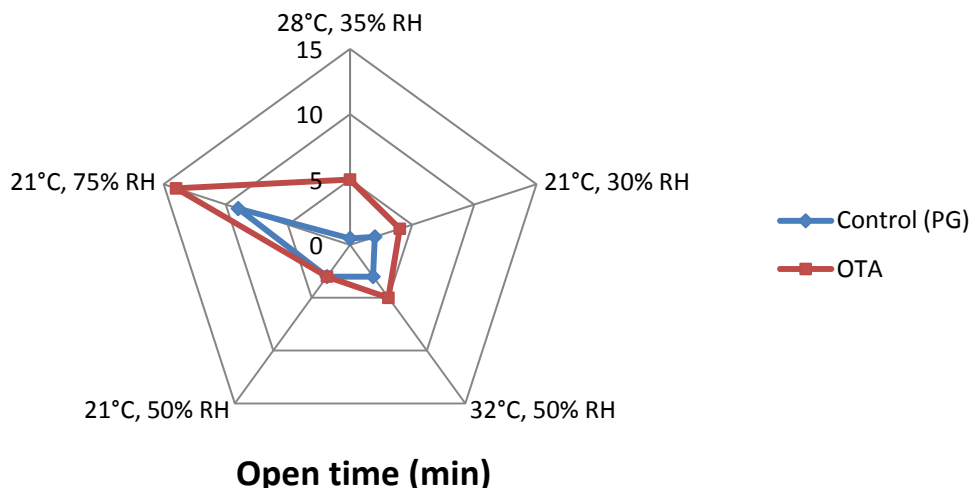
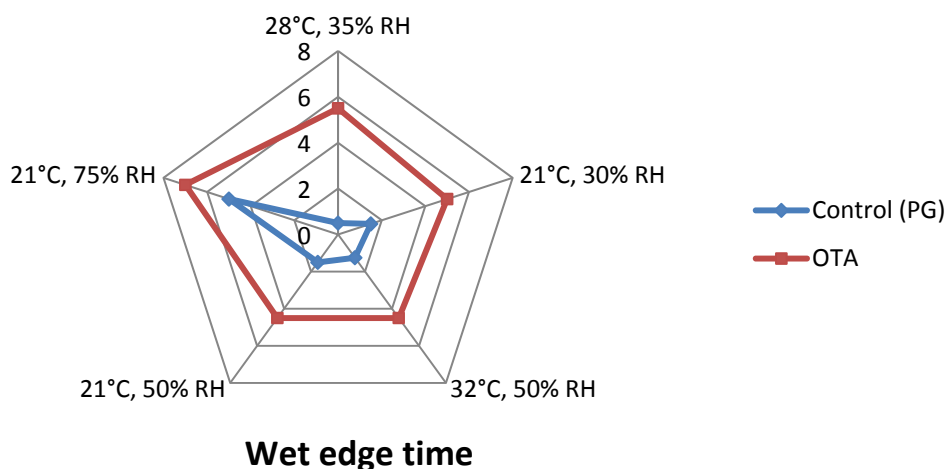


Figure 5. Weight loss over 60 minutes for control paint at 25°C and relative humidities of 20, 50, and 80%

Open and wet edge times were evaluated on both the control and experimental paint containing the OTA at five different temperature / humidity combinations in an environmentally controlled chamber. Figure 6a is a spider chart that provides a comparison of the wet edge times as a function of conditions, while 6b is an analogous comparison of the open time. As expected, the humectant propylene glycol in the control paint provides poor wet edge / open time at low temperature / low humidity and good wet edge / open time at high temperature / high humidity. In contrast, the paint with the OTA provides excellent wet edge time regardless of temperature and humidity. Open times were superior for the lower VOC paints containing the OTA except at 32°C and 50% RH, where the results were relatively similar.



Figures 6 a-b. Results of workability testing for a control paint with propylene glycol and a paint with OTA at a variety of environmental conditions in terms of wet edge time (a) and open time (b)

A novel rheology technique has been developed at Eastman Chemical Company to evaluate the drying and solidification processes of liquid films<sup>12</sup>. The device may be adapted for use with conventional commercial rheometers, and consists of a small T-bar probe that is partially submerged in a shallow trough of coating (see Figure 7). As the coating dries, the complex viscosity behavior of the drying film may be observed.



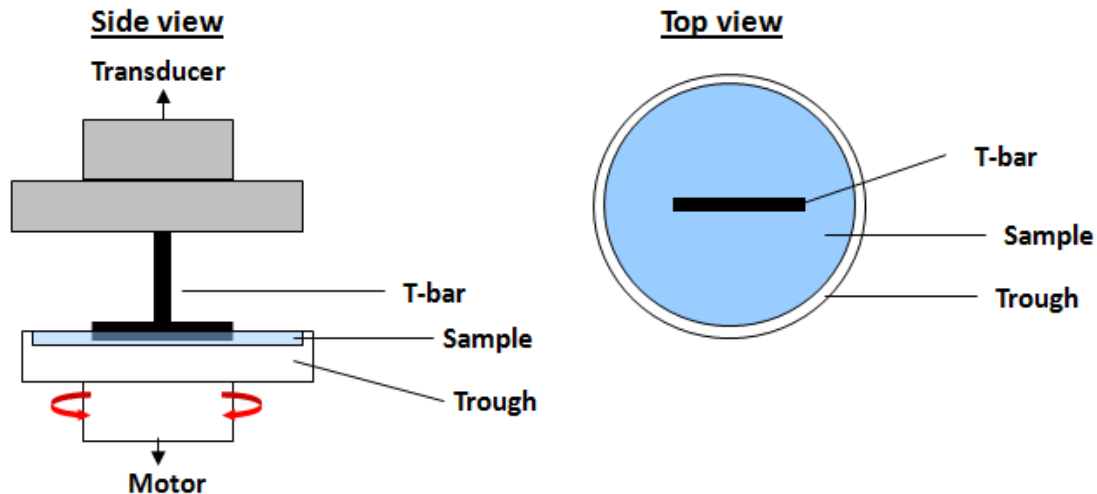


Figure 7. Depiction of equipment utilized to measure rheology during solidification of liquid coatings

A modification of this rheology method was utilized to study the drying and rewetting behavior of paints to simulate wet edge / open time testing. For this testing, approximately 0.5 mL of a paint sample was added to a 70  $\mu\text{m}$  trough and doctored to the rim using a scraping knife edge from Precision Gage & Tool Company. The T-bar probe was then immersed in the paint to 50  $\mu\text{m}$  from the bottom of the trough. A dynamic time sweep at a fixed frequency of 25 rad/sec with 25% strain was run on the AR-2000 rotational rheometer from TA Instruments. Testing began about 40 seconds after the initial introduction of the paint to the trough. At fixed times, the drying paint was rewetted with a few additional drops of paint using a hypodermic syringe. This allowed the rewetting behavior of each coating sample to be quantified. The coatings investigated were based on the formulation from Table I using propylene glycol (PG) at 3% and 6% loadings as the conventional, high VOC humectant, 3% of a commercial 400 molecular weight polyethylene glycol (PEG) as a low VOC humectant, and 3% of the OTA on an actives basis.

Figure 8 provides a comparison of the four paints with rewetting at four minutes (240 seconds). The viscosity increases until the point at which additional paint is introduced to the trough, at which point the paint thins back out. The paints with 3% OTA had a 75% reduction in viscosity with the addition of more paint, followed closely by the 6% PG (62% reduction), 3% PG (50% reduction), and 3% PEG (21% reduction). This suggests that the paint containing PEG is no longer open after four minutes. Figure 9 provides an analogous look at the four paints with rewetting at five minutes (300 seconds). The viscosities prior to rewetting were significantly higher after five minutes. The sample containing 3% OTA builds viscosity rapidly, which may be associated with improved sag resistance, while still rewetting as evidenced by an 82% reduction in viscosity. The other three paints showed minimal reduction in viscosity upon rewetting at five minutes (15 – 20%), which suggests that it is unlikely that these paints could be reworked to any significant extent. These viscosity traces correspond closely to open time measurements that were made concurrently in the rheology lab, which yielded 7.5 minutes open time for the paint with 3% OTA, 5.5 minutes for the paint with 6% PG, 4 minutes for the paint with 3% PG, and 3.5 minutes for the paint with 3% PEG. Shear rate sweeps were measured on each of the paints, and the viscosity at a shear rate of 0.01  $\text{sec}^{-1}$  was found to increase in the order of 3% OTA < 3% PEG < 6% PG < 3% PG. Equation 1 suggests that if

all other parameters were equal that a higher  $\eta_0$  would yield a higher  $\rho_{cap}$ , which has been associated with improved open time. These paints clearly do not follow this trend, since another variable in Equation 1 may be changing or the coalescence process may be altered by the presence of some of these additives.

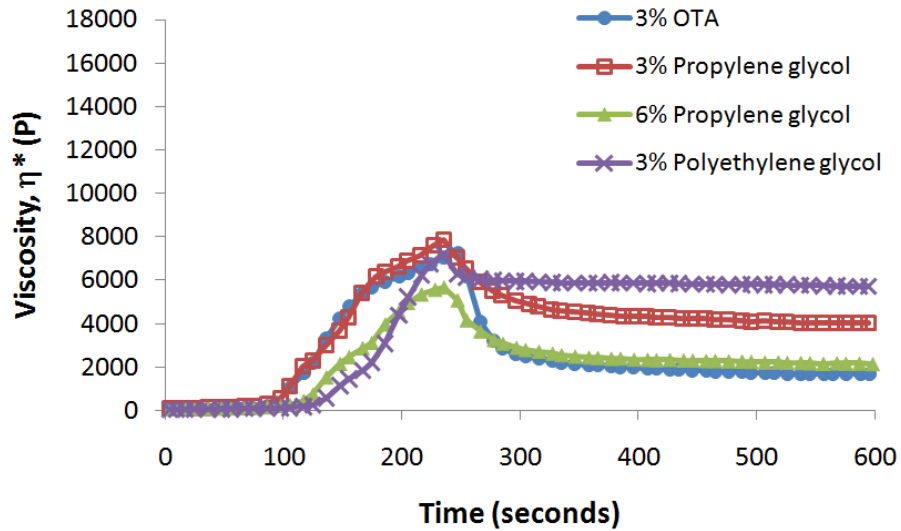


Figure 8. Complex viscosity traces of paints rewetted after 240 seconds as measured by drying rheology

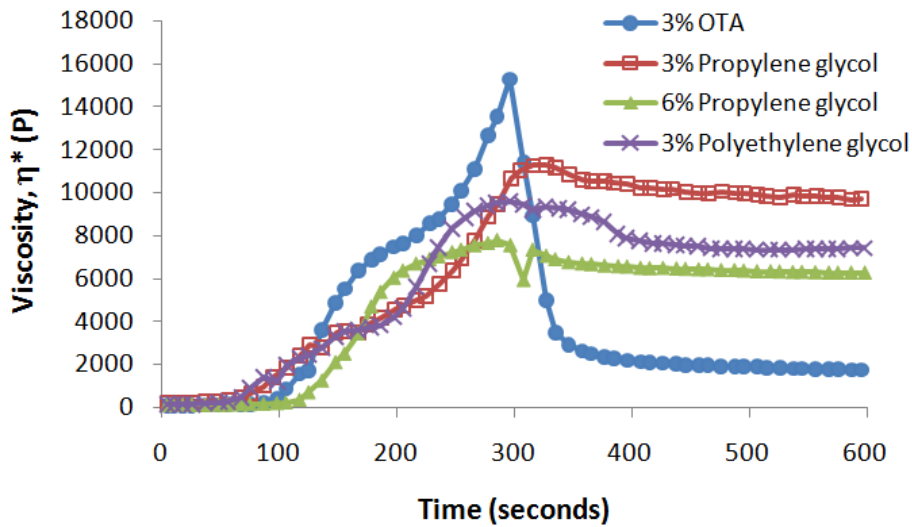


Figure 9. Complex viscosity traces of paints rewetted after 300 seconds as measured by drying rheology

Figure 10 provides a comparison of the viscosity traces for paint samples containing 3% OTA that were rewetted at a series of times including 4, 5, 6, and 8 minutes. From this chart, it is evident that viscosity prior to rewetting increases with increasing dry time. Beyond 5 minutes, the viscosity after rewetting continues to increase, but even after 8 minutes, there is still more than a 60% reduction in viscosity after additional paint is added to the drying film. This suggests that the OTA provides improved workability through a unique mechanism beyond that of simply reducing the evaporation rate of the continuous phase. Further investigation will be required in order to better elucidate this phenomenon.

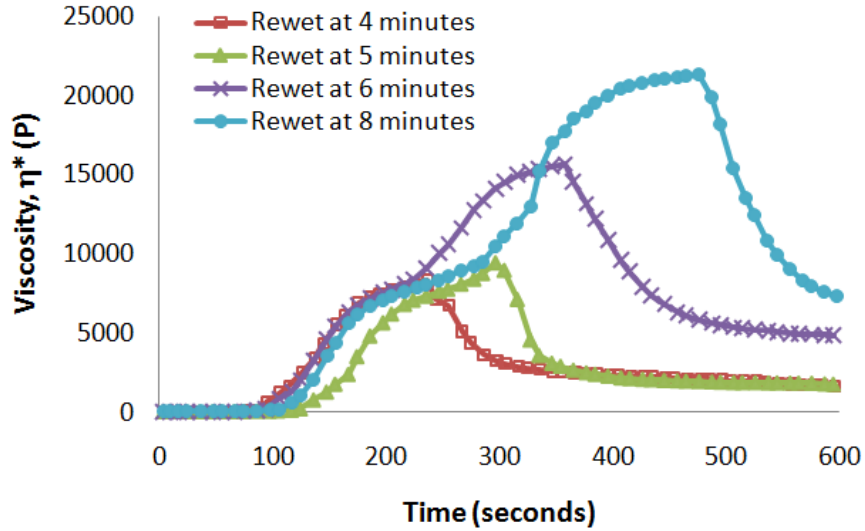


Figure 10. Complex viscosity traces of paint with 3% OTA rewetted after 4, 5, 6, and 8 minutes

The rewetting behavior of the control paint with 3% PG and the paint with 3% OTA was further studied using a variant of the open time test method illustrated previously in Figure 2. At each time period, instead of using the typical four cycles with the paint brush when rewetting, the paints were brushed until the edge could be worked in (up to a maximum of 50 cycles). Figure 11 provides a summary of the results for both the wet edge (left) and open time (right). It is evident that the paints with 3% PG require more strokes to eliminate the wet edge, and beyond 6 minutes the edge can no longer be worked in. The wet edge of the paint with 3% OTA can still be worked in after 12 minutes. Results were similar for the multiple cycle open time testing. Paint formulated with the OTA exhibits typical viscosity development characteristics, but the paint can be rewetted and reworked without negatively impacting recoat time.

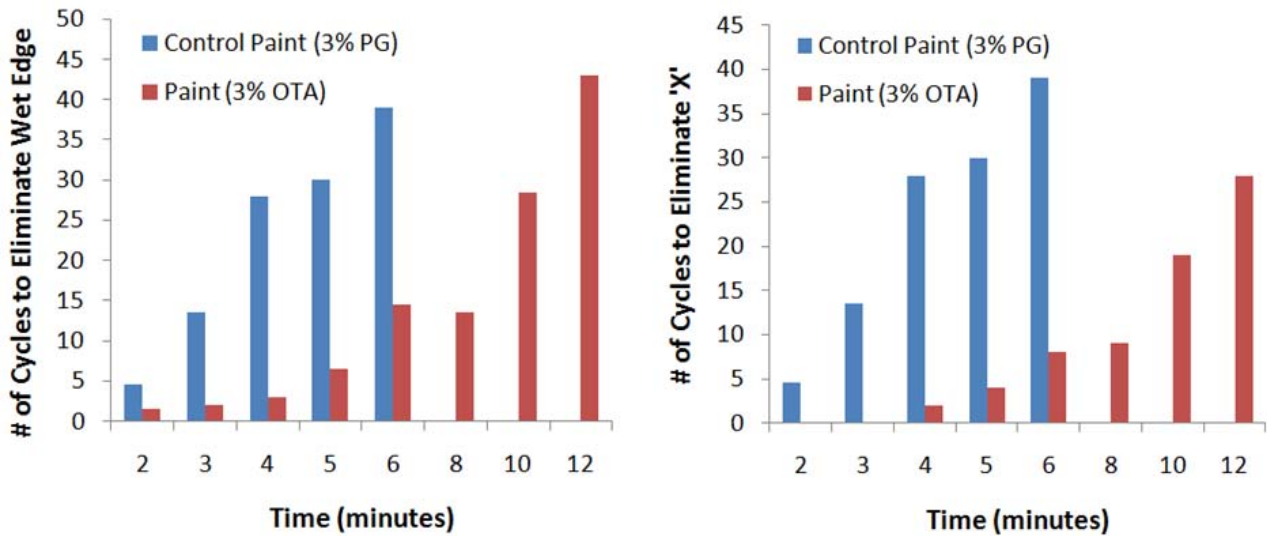


Figure 11. Workability testing for a control paint with PG and a paint with OTA in which the number of strokes required to eliminate the wet edge (left) and eliminate the open time 'X' (right) were determined

## Conclusions

The purpose of this research was develop a low VOC additive that would improve wet edge and open time of latex paints without compromising paint performance. A candidate material was identified based on the combination of an initial screening process with more extensive formulation and testing work in conjunction with a large designed experiment. The open time additive was demonstrated to provide more robust workability over a range of temperature and humidity as compared to propylene glycol, which is a conventional high VOC humectant. A novel rheological technique was utilized to follow the drying and rewetting behavior of a series of paints. Paint formulated with the open time additive exhibited a typical viscosity increase during the early stage of drying, but was unique in that the paint film would thin back down remarkably upon rewetting with several drops of fresh paint. This rewetting behavior was further examined by open time and wet edge testing in which samples were brushed until the edge or 'X' could be eliminated. Paint formulated with propylene glycol could only be reworked for about 5 minutes, while paint with the open time additive could be rewetted and reworked up to 12 minutes. The mechanism for this behavior is not fully understood, but the early part of the coalescence process may be altered by the presence this additive. Further studies are required in order to better elucidate this phenomenon.

## References

- [1] Andrews, M. D., *J. Paint Technol.*, **1974**, 46 (598), 40.
- [2] Sullivan, D. A., *J. Paint Technol.*, **1975**, 47 (610), 60.
- [3] Croll, S. G., *J. Coat. Technol.*, **1986**, 734 (58), 41.
- [4] Winnick, M. A.; Feng, J., *J. Coat. Technol.*, **1996**, 852 (68), 39.
- [5] Salamanca, J. M.; Ciampi, E.; Faux, D. A.; Glover, P. M.; McDonald, P. J.; Fouth, A. F.; Peters, A. C. I. A.; Satguru, R.; Keddie, J. L., *Langmuir*, **2001**, 17, 3202.
- [6] Routh, A. F.; Russel, W. B., *AIChE J.* **1998**, 44 (9), 2088.
- [7] Monaghan, G., *JCT Coat.*, **2007**, 4 (10), 30.
- [8] Akkerman, J.; Bosma, M.; Berry, A.; Fallani, F.; Adolphs, R.; Mestach, D., *Surf. Coat. Aus.*, **2010**, 47 (1/2), 13.
- [9] Browning, W.; Mestach, D.; Pilaszak, W.; van Egmond, R.; Bosma, M.; Rensen, E., *Surf. Coat. Aus.*, **2008**, 45 (1/2), 12.
- [10] Molenaar, F.; Svanholm, T.; Toussaint, A., *Prog. Org. Coat.*, **1997**, 30, 141.
- [11] Lofflath, F.; Gebhard, M., *J. Coat. Technol.*, **1997**, 867 (69), 55.
- [12] Seo, K. S.; Posey-Dowty, J. D, US 7,185,530 B2 and US 7,472,584 B2.