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A New Era in Superwetters

for Waterborne and UV-Curable Coatings and Inks

The growth today in waterborne and radiation-cured coatings and inks far exceeds that of its solventborne equivalents. The need for lower VOCs, “greener” materials, improved food safety and reduced economics (inventory reduction and faster production speeds) all contribute to this growth, and this in turn increases the need for superwetters. Why? As formulators transition from solventborne coatings and inks to create healthier, safer and more eco-friendly systems, performance requirements bring to light issues and disadvantages associated with waterborne and radiation-curable systems. In particular, many of the surfactant packages utilized have the negative effect of stabilizing foam from air incorporation during coatings production and application. In addition, in waterborne coatings specifically, the inherent high surface tension of water creates the potential to cause surface defects such as craters and poor wetting on substrates.

With the growth of waterborne and radiation-curable coatings and inks comes the development of more binder systems, and formulators find they require a wider portfolio of wetting additives to choose from when developing new formulations. No one, universal solution is suitable across a wide range of formulations and substrates because inconsistent performance; lack of regulatory compliance; poor pH stability; poor performance in demanding, high-speed applications; and cost all bring the formulator problems. In the coating and ink industries, silicone materials have been developed and used for many years to improve the surface appearance and properties of many systems, including wetting, but this technology has also suffered from inconsistent performance. Dow Corning has recently launched four 100% silicone polyether co-polymers with good compatibility in waterborne and radiation-curable systems to provide good substrate wetting consistently over a wide range of formulations, pH ranges and substrates.

This article describes an application study comparing the performance of these four unique silicone polyether co-polymer superwetters to commercially available surfactants on

the market (acetylenic diols and silicone polyether copolymers, including Gemini surfactants) (Table 1).

Superwetters

The new superwetters are 100% silicone polyether copolymers, consisting of a hydrophobic, methylated, short-chain silicone backbone with pendant hydrophilic ethylene oxide chains. The ethylene oxide chains are end-capped with hydrophilic organic groups such as hydroxy, methoxy or acetoxy. In this study they were evaluated in aqueous solution, a waterborne polyurethane-based wood parquet lacquer coating, waterborne acrylic-based flexo gravure ink and in UV acrylate coatings (Table 2).

These new superwetters are low-viscosity and low-molecular-weight materials, and so are easy to incorporate into coat-

TABLE 1 | Commercially available wetting surfactants used to benchmark superwetters.

Competitor	Chemistry
1	Acetylenic diol in solution
2	Silicone polyether co-polymer in solution
3-5, 7-9	Silicone polyether co-polymer
6	Silicone polyether co-polymer (Gemini)
10-15	Fluorosurfactants

TABLE 2 | Hydrophilicity and reactivity (end capping) of the four superwetters.

Product Name	HLB E0	End-Capped
Dow Corning 67 Additive	11.5	OH
Dow Corning 500W Additive	10.7	OAc
Dow Corning 501W Additive	10.6	OMe
Dow Corning 502W Additive	13.2	OH

TABLE 3 | Static surface tension of superwetters at 0.1% by weight in water.

Product Name	Static Surface Tension (mN/m)
Water only	71.0
Dow Corning 67 Additive	21.1
Dow Corning 500W Additive	22.0
Dow Corning 501W Additive	20.5
Dow Corning 502W Additive	22.4

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FIGURE 1 | Dynamic surface tension, 0.2% by weight surfactants in water.

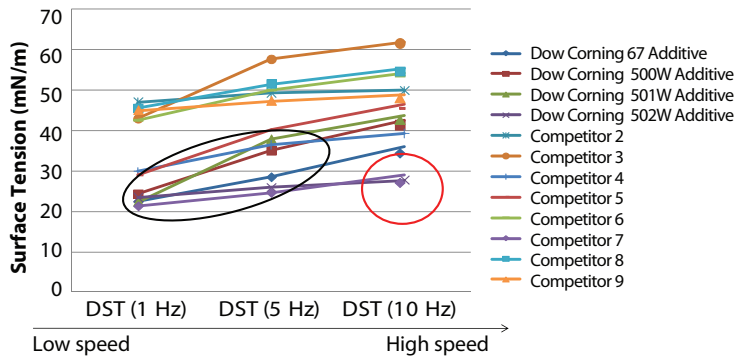


FIGURE 2 | Dynamic surface tension of all surfactants at pH 11 (0.4% by weight in water).

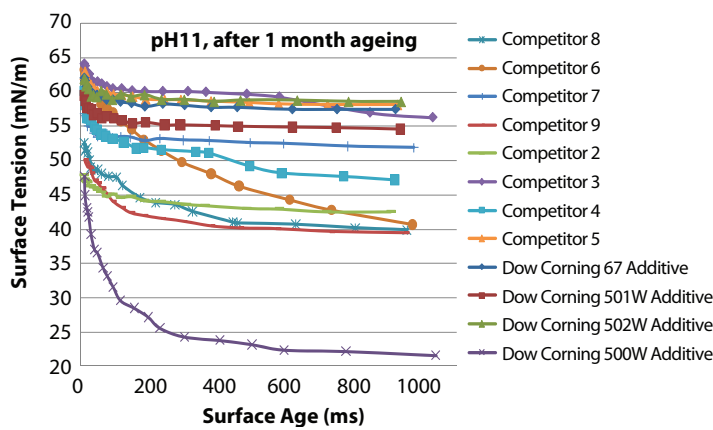


FIGURE 3 | Surface appearance in the waterborne wood parquet coatings shown in Tables 4 and 5.

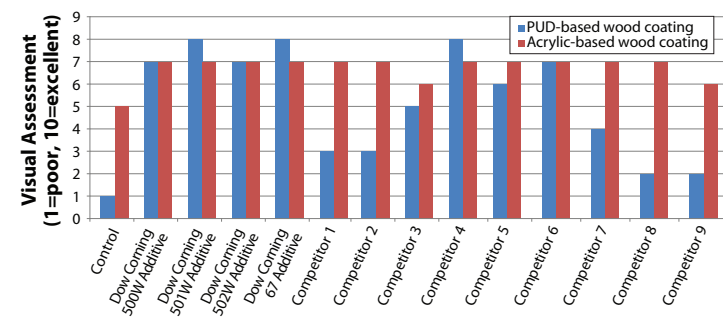


FIGURE 4 | Surface appearance of a waterborne polyurethane acrylic wood parquet lacquer with and without Dow Corning 67 Additive (added at 0.2% by weight in the total formulation).



ings and inks. They migrate quickly to, and pack efficiently at, the coating surface, giving rise to low surface tension required to achieve good wetting performance. Static surface tension measurements were conducted with 0.1% by weight aqueous solutions at room temperature. The equilibrium surface tension was measured with a Krüss K10T tensiometer and a platinum Wilhelmy plate. For this test method, a platinum plate is immersed in the test liquid and the force required to remove the plate from the solution is taken as a measure of the surface tension of the liquid.

The superwetters provide excellent static surface reduction (Table 3). While the ethylene oxide content (HLB) doesn't influence the surface tension directly in water, this can affect the solubility and therefore performance of the surfactant in a coating or ink formulation. Therefore, having a range of HLB values allows the formulator to choose the right product for a given formulation.

While static surface tension will give a theoretical indication of how much a surfactant can reduce the surface tension of a given solution to achieve good wetting, Dynamic Surface Tension (DST) is more reflective of real-life performance in a coating or ink application process, as this measures how quickly a surfactant migrates to the air/liquid interface to do its work. Figure 1 shows DST results of the superwetters and competitor surfactants at 0.2% by weight in water. DST is measured by using a bubble tensiometer that bubbles air through the test liquid at an increasing rate, during which the maximum pressure that is required to form a bubble is measured. As the bubble rate increases from 1 bubble per second to 10, the time to create the new interface (liquid/air) decreases.

All of the superwetters perform well at low to medium application speeds, as indicated by low DST at 1 and 5 Hz. In particular, Dow Corning® 502W Additive and competitor additive 7 maintain their very low DST at high speed. This gives an indication that both products will be useful for wetting in high-speed applications and challenging conditions such as spraying. However, this test is only an indication and does not reflect real-life performance in all cases, and we will see later that while the performance of Dow Corning 502W is supported with consistent application data, this is not the case for the competitor 7 additive.

High-pH paints are most common in the decorative market, and here, long-term stability of a wetting additive is key. Figure 2 shows the DST performance of the surfactants at pH 11 after 1 month aging. Long-term performance of Dow Corning 500W Additive at pH 11 was achieved after 1 month aging, providing low surface tension consistently. This allows the formulator to use it in high-pH formulations with confidence of long-term wetting performance at the end-use stage. The data indicates that this additive achieves long-term performance at high pH due to the stability of the non-reactive acetoxy-end capped group.

Benefits of Superwetters

In this part of the application study, each surfactant was compared at 0.2% by weight in each formulation. The following properties were evaluated to compare performance:

1. Surface appearance by visual assessment of surface defects (wetting and leveling);
2. Slip (coefficient of friction).

With the addition of surfactants to a formulation comes the risk of foam stabilization, and the impact on foaming was evaluated by measuring foam height after high-speed shearing.

Performance in Waterborne Polyurethane and Acrylic Wood Parquet Lacquer Formulations

The two typical wood coating formulations shown in Tables 4 and 5 were used to evaluate the performance of the superwetters. The first is based on a polyurethane dispersion, the second on an acrylic dispersion.

In Figure 3, we can see the assessment of these wood coatings on glass with both the superwetters and competitive surfactants 1-7. Glass is used as the substrate since this is the standard substrate used in the industry to evaluate wood coatings. The wetting performance of the superwetters is high, with only some small differences between the products. Comparing these to competitive additives 1-7, we can see that the wetting performance of the superwetters is, for the most part, better than the competition. More importantly perhaps is that performance is consistent across both formulations, and while some competitive additives perform well in one formulation, performance is poor in the other.

The old adage, “seeing is believing”, is certainly true in the case of the superwetter performance. Figure 4 shows the wetting performance of the waterborne polyurethane acrylic wood parquet lacquer with and without a superwetter; in this example Dow Corning 67 Additive is shown.

Performance in UV-Curable Formulations

Dow Corning’s new superwetters can be used in radiation-cured coatings, whether in waterborne, solventborne or solventless delivery systems. Figure 5 demonstrates the performance of a waterborne, radiation-curable coating on PVC, a low-energy and difficult-to-wet substrate.

Again the superwetter family shows consistent performance for wetting, and there is little or no impact on the slip properties of the coating. No negative impact on slip can of course be critical to some applications, such as flooring coatings, but where increased slip is required

TABLE 4 | Waterborne polyurethane acrylic wood parquet lacquer formulation.

Ingredients	Percent by Weight
NeoPac® E-106: Aromatic(anionic) urethane acrylic copolymer dispersion	91
Butyl diglycol	4
Aquacer® 593:	5
Wax emulsion (modified polypropylene)	
Total	100

TABLE 5 | Waterborne acrylic wood parquet lacquer formulation.

Ingredients	Percent by Weight
Joncryl® 8383: semi-translucent emulsion and self-crosslinking acrylic polymer emulsion	91
Texanol	6
Aquacer 593:	
Wax emulsion (modified polypropylene)	3
Total	100

this can be modified using another additive from the Dow Corning additives portfolio. This is demonstrated in Figure 6, where the performance of Dow Corning 67 Additive has been compared to Dow Corning 57 Additive in a solventless UV-curable coating. In this formulation we can see that the 67 Additive gives the superior wetting performance with no impact on slip (coefficient of friction), while the 57 Additive gives a lower wetting performance but with a dramatic decrease in slip. This differentiation in slip performance between the superwetters and other additives gives formulators the choice to customize their formulation to suit the end application.

FIGURE 5 | Surface appearance and dynamic coefficient of friction in waterborne UV-curable coating at 0.2% by weight in the total formulation.

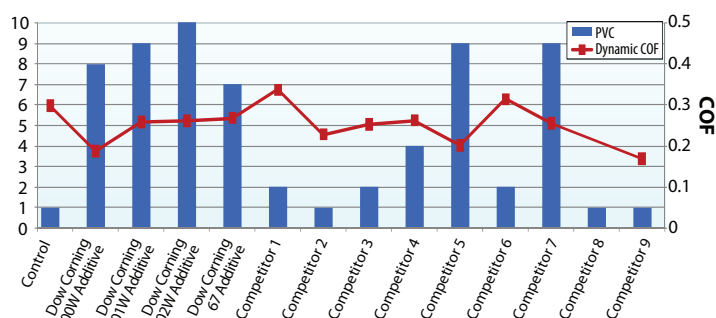


FIGURE 6 | Wetting (by droplet diameter) and dynamic coefficient of friction with Dow Corning 57 and 67 Additives in solventless UV-curable coating at 0.2% by weight in the total formulation.

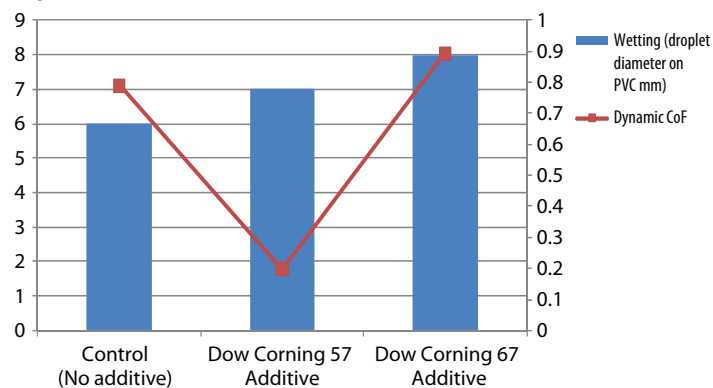
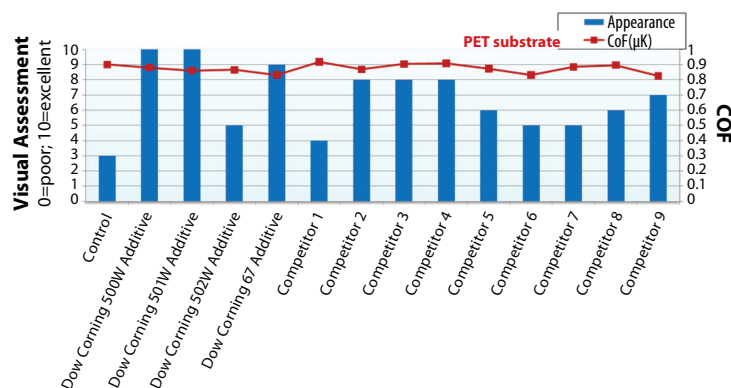


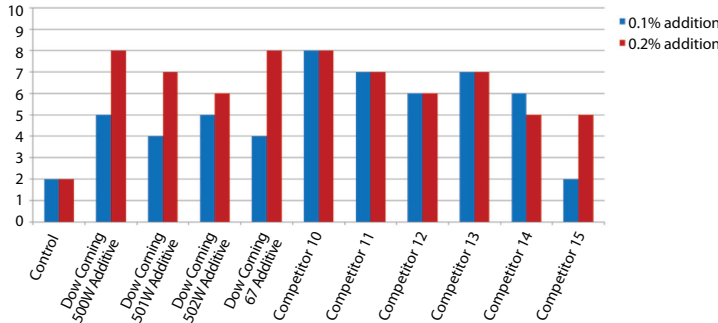
FIGURE 7 | Surface appearance and dynamic coefficient of friction of waterborne flexographic ink on PET at 0.2% by weight in the total formulation.



Performance in Waterborne Flexographic Ink

In this example on PET (Figure 7), another low-energy substrate that is very difficult to wet, Dow Corning 500W and 501W Additives excel in performance, an indication that the non-reactive end capping is influencing the per-

FIGURE 8 | Surface appearance of superwetters versus fluorosurfactants in waterborne wood parquet coatings. Comparison is made at 0.1 and 0.2% by weight in the total formulation.



- A higher addition level of the Dow Corning Superwetters is required to give the same performance as the fluorosurfactants.
- However on a cost-in-use basis they can be competitive, exemplified here with both Dow Corning 500W Additive and Dow Corning 67 Additive.

FIGURE 9 | Foaming and surface appearance in waterborne flexographic gravure ink at 0.2% by weight in the total formulation.

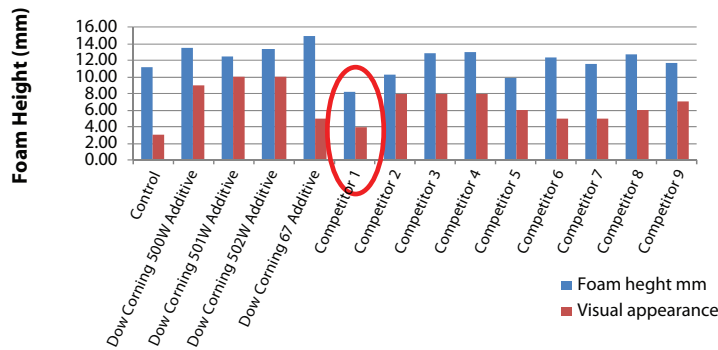
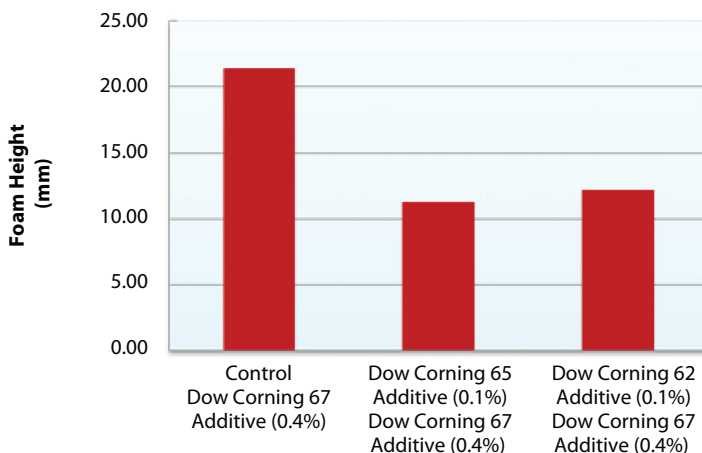


FIGURE 10 | Foaming in waterborne flexographic gravure ink at 0.4% by weight Dow Corning 67 Additive and Dow Corning 62 or 65 Additive in the total formulation.



formance. The coefficient of friction remains unchanged; this can be particularly important in printing applications where high slip results in difficulties in stacking printed items. Again, if a reduction in the slip properties is required, this can be adjusted using a customized slip additive such as Dow Corning’s 57 or 51 Additive. This differentiation in slip performance between the superwetters and these other additives gives formulators the choice to customize their formulation to suit the end application.

Fluorosurfactants

While constantly under scrutiny for their bio persistence, fluorocarbon-based surfactants are still used in coatings and inks today. Effective at very low addition levels, they are also high in cost. As an addition to this study, we have evaluated six commercial fluoro-based surfactants (competitors 10-15) versus the superwetters. Figure 8 demonstrates the performance at 0.1 and 0.2% by weight to the total formulation in the waterborne polyurethane-based lacquer shown in Table 4. While a higher addition level of the superwetters is required to give the same performance as the fluorosurfactants, on a cost-in-use basis they can be competitive, exemplified here with both Dow Corning 500W and 67 Additives.

Foam Stabilization

While the addition of surfactants achieves wetting on difficult-to-wet substrates, they potentially also have a negative effect on foam behavior of inks and coatings in some cases, leading to foam stabilization during production and application at high shear. This is true for all types of chemistries used.

The effect of these surfactants on the foaming property of a waterborne flexographic gravure ink was measured by evaluating foam height after high-speed shearing. In Figure 9 we can see that some foam stabilization is evident with both the superwetters and competitive additives. Where the surfactant does the best job it unfortunately results in the highest amount of foam – but conversely, low foam stabilization cannot compensate for poor wetting!

Important to the formulator is that this foam can be controlled. Figure 10 clearly demonstrates that with addition of Dow Corning defoamers at only 0.1% by weight to the total formulation, we see a reduction of foaming.

Conclusion

Dow Corning’s superwetters are effective in providing consistent coating performance in a wide range of formulations. In particular, our 500W Additive provides excellent performance with high pH stability, and our 502W Additive is especially suitable for very high-speed printing and challenging spray applications. Coatings formulators can select superwetters based on their different performance needs to get consistent product performance. ■

References

1. Aquacer® is a registered trademark of BYK Additives and Instruments.
2. NeoPac® is a registered trademark of DSM Neoresins+.
3. Joncryl® is a registered trademark of BASE.
4. Texanol® is a registered trademark of Eastman.
5. M.R. Porter, Blackie, Handbook of Surfactants, USA; Chapman & Hall, New York.
6. Owen, MJ, The Surface Activity of Silicones: A Short Review, *I&EC Prod. Res. Dev.*, 10 (1980), 97.
7. W.H. Pushaw III, Handbook of Coatings Additives, (L.J. Calbo, ed.), Marcel Dekker, Inc., New York, 1987, p.271.
8. Carbinol Functional silicon-based technologies for coatings, Donna Perry, Vicky James, Gerald Witucki.
9. <http://www.chinasilicone.com/Modified-polyether-trisiloxane.html>
10. <http://www.cosmeticsandtoiletries.com/formulating/ingredient/surfactant/114203679.html>