

# Smooth Operators: Wetting, Flow, and Leveling and Dispersing Solutions for UV Cure Coatings

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## **Abstract:**

The benefits of solvent free UV EB coatings are well documented. The absence of solvent however presents some challenges for formulators. Specifically, wetting, flow, leveling in unfilled coatings, dispersing in pigmented and thixotropy in filled systems present difficulties due to wide variety of substrates used and fast cure of UV/EB coatings systems. This paper will discuss the underlying causes and present solutions to each of these challenges with specific examples.

## **INTRODUCTION:**

UV-EB cure technology offers increased productivity, lower energy consumption and environmental advantages<sup>1</sup>. Therefore, formulators and end-users prefer formulation systems based on UV-EB curable systems compared to conventional water or solvent based technologies as evidenced by their increasing use in coatings, inks and adhesive applications. The growth in the number of applications and the variety of substrates, example thermoplastic polyolefins (TPO) in automotive and metallized plastics in mobile handsets requires UV curable formulations to possess special properties for specific end uses<sup>2,3</sup>. First some basic definitions:

**Wetting:** This refers to the process by which a liquid coating displaces air at the air-substrate interface.

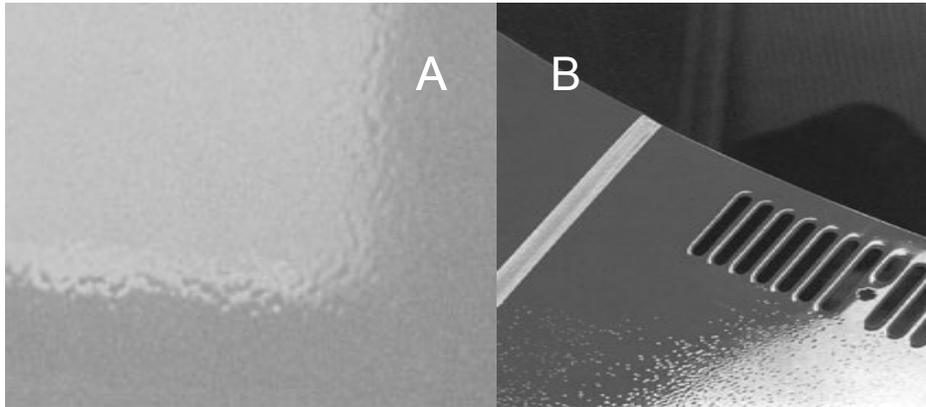
**Flow:** This refers to the motion of the coating on a substrate during and after wetting.

**Leveling:** This refers to the surface aspect of the coating after wetting and before curing.

**Dispersion stability:** The ability of a dispersant to wet out pigment and keep pigment particles from agglomeration and prevent settling.

**Pseudoplasticity and Thixotropy:** Pseudoplastic is shear dependent viscoelastic flow. This is seen as a reduction in viscosity with increasing shear rate. A material is thixotropic when in addition to shear strain rate there is time dependent response, ex. an ink's viscosity changes with time even after shear forces are removed<sup>4</sup>.

Substrate wetting and flow are important for all coatings to ensure good protective functions (good adhesion, resistance to ingress of moisture and other environmental agents) and aesthetic appeal (smooth surface appearance). Typical problems encountered due to poor wetting are cratering or crawling and fish eye like appearance on portions of the coatings (Fig. 1)



**Figure 1: Top coat wetting & flow challenges: (A) “Orange peel” effect and (B) “Cratering”**

Poor flow and leveling and high coating viscosity can occur due to sub-optimal pigment dispersion. Improper pigment stabilization can result in agglomeration and settling can lower coating gloss. In filled topcoats, one encounters increased thixotropy which create problems during the application process and reduces surface appeal. Finally poor flow and leveling can cause an “orange peel” like effect (Fig.1), produce surfaces that are harder to sand evenly and create poor surface appearance. This is especially true for fast curing UV/EB coatings, if curing line speeds are so high that the coating does not fully flow and level out prior to cure, after which time, the morphology of the coating is “frozen” or irreversible due to rapid crosslinking. Using four examples we examine how formulators tackle these issues in practice

### **Experimental and Materials:**

**Contact angle:** Contact angle measurements were done using a Ramie-Hart Goniometer at 25 °C. All measurements were made by placing a single drop of material on a Teflon substrate. The dynamic surface tension of the different UV-acrylates was measured at 25 °C using a Krüss maximum bubble pressure tensiometer BP 2, in combination with a BPC2 capillary and BP23 software.

**Viscosity:** The viscosity of all monomers was measured using a Brookfield DVII Plus viscometer at 25 °C.

### **Rheology:**

The apparent viscosity of the inks was measured using Bohlin-Rheometer RVO from at 25 C using an oscillatory shear strain rate range of 0.1 to 1000 s<sup>-1</sup>.

**Curing conditions:** All coatings, were cured as noted in tables provided for the formulations in the results and discussion section.

**Gloss:** Gloss measurements were made using a BYK Gardner Micro-Tri-Gloss meter. All gloss readings were taken at 60°.

## Materials

All starting materials unless otherwise noted were obtained from Cognis Corporation.

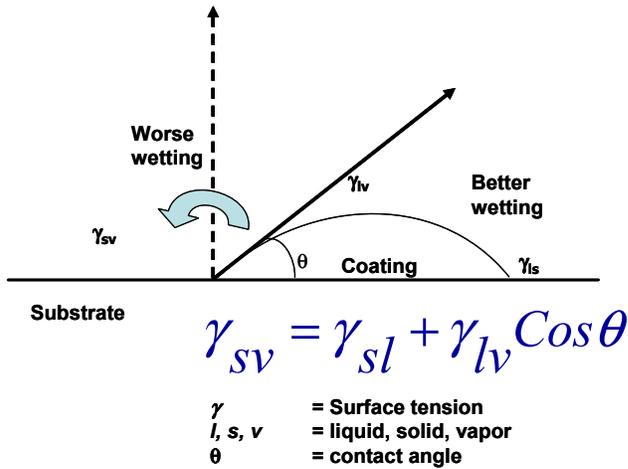
**Table 1: Descriptions of monomers and oligomers used in this study**

Product abbreviation	Chemical Description
DPGDA	Dipropyleneglycol diacrylate
TPGDA	Tripropyleneglycol triacrylate
HDDA	Hexanediol diacrylate
EOHDDA	Ethoxylated hexanediol diacrylate (2 EO)
POHDDA	Propoxylated hexanediol diacrylate (2 PO)
GPTA	Propoxylated glycerol triacrylate (3.8 PO)
PONPGDA	Propoxylated neopentylglycol diacrylate (2PO)
EONPGDA	Ethoxylated neopentylglycol diacrylate (2EO)
TMPTA	Trimethylol propane triacrylate
PEOA	Ethoxylated phenol acrylate (2.5PO)
POTMPTA	Propoxylated trimethylol propane triacrylate (3PO)
3EOTMPTA	Ethoxylated trimethylol propane triacrylate (3EO)
7EOTMPTA	Ethoxylated trimethylol propane triacrylate (7EO)
14EOTMPTA	Ethoxylated trimethylol propane triacrylate (14EO)
IDA	Isodecyl acrylate
PEA -1	Polyester acrylate
UA-1	Urethane diacrylate
UA-2	Urethane diacrylate
TPG-OMeA	Tripropyleneglycol methylether acrylate
NPG(2PO)-OMeA	Propoxylated neopentylglycolmethylether acrylate
BDGGDA	Acrylated Bisphenol A diglycidyl ether
SF73	Polyurethane polymer dispersant
S71UV	Acrylated polysiloxane block polymer
P61	Polyurethane polymer dispersant
Amine acrylate	Amine acrylate
BPA(4EO)DA	Ethoxylated Bisphenol A

## Results and Discussion

### Case I Clear coat on Tin Metal

This formulation refers to a coating on untreated or “oily” tin metal. The requirement in this case was UV curable coating of sprayable viscosity for tin metal without a pre-treat cleaning step which after cure had good adhesion to metal and excellent surface appearance. Optimum substrate wetting is very important for all industrial-coating processes. For best substrate wetting, the contact angle  $\theta$  made by the coating onto the substrate, should be as low as possible (Figure 2).



**Figure 2. Contact angle and Young’s equation for surface tension**

In other words, the surface tension of the liquid coating should be lower than the surface energy of the substrate to be coated. A typical way of achieving this is to treat the substrate with plasma, corona or flame (usually applied to plastics or other chemical treatments (usually applied to metals) to clean and increase the surface energy of the substrate. This was not an option in our case. So we chose an alternative, i.e. to reduce the surface tension of the coating formulation.

**Figure 3. Contact angle on Teflon® for a series of UV curable monomers**

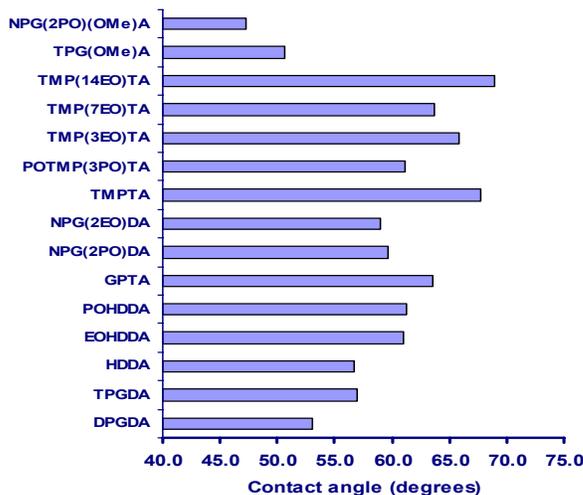


Figure 3 shows the contact angle measurements for a series of UV curable monomers on poly(tetrafluoroethylene) (Teflon®). This substrate due to its extreme hydrophobicity present severe wetting challenges for any coating. So, lower the contact angle of a monomer on Teflon®, we surmised that better should be its wettability on other surfaces with higher surface energy than Teflon®. From Figure 3, the three monomers with lowest contact angles were acrylates of NPG(2PO)-OMe, TPG-OMe and DPG.

Similarly, a survey of viscosity and surface tension data of various monomers (Table 2), showed that the surface tension of monomers bearing propoxylate groups was consistently lower than those bearing ethoxylate groups.

**Table 2: Low Surface Tension Monomers**

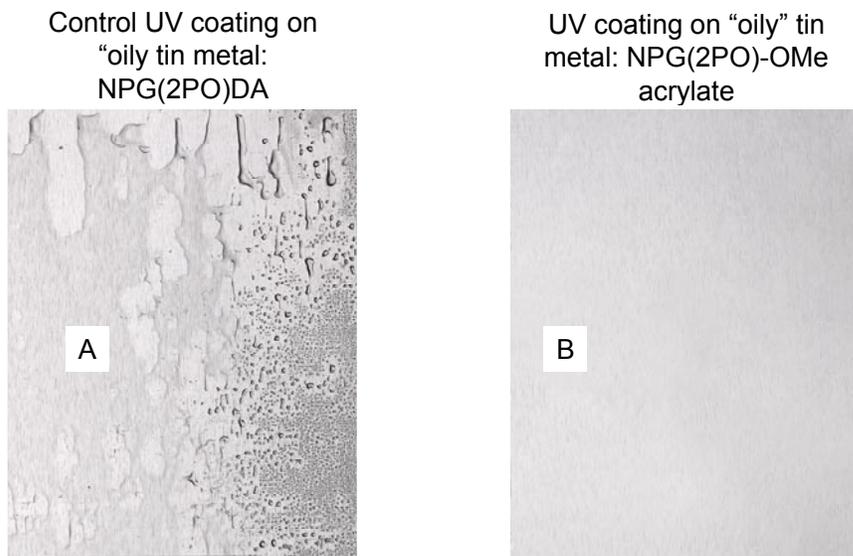
Monomers	Surface tension (mN/m)	Viscosity (mPa.s)
NPG(2PO)DA	31.5	15
TMP(3PO)TA	33.0	100
GPTA	35.2	90
Above are low viscosity but surface tension is still > 30 dynes/cm		
Below mentioned monomers are lower in viscosity and surface tension		
NPG(2PO)-OMe acrylate	28.2	8
Isodecyl acrylate	28.7	8

**Table 3: Clear Coating Formulation on Tin Metal**

Product	Description	%
PEA-1	Tetrafunctional polyester acrylate oligomer	30
UA-1	Aliphatic urethane diacrylate oligomer	10
NPG(2PO)-OMe monoacrylate	Wetting and flow & leveling monomer	12
EOHDDA	Reactive diluent	43
2-Hydroxy-2-methyl-1-phenyl propanone	Photoinitiator	5
<b>Total</b>		<b>100</b>
Cure conditions: RDS Rod #5; 10µm wet film thickness; 15m/min; 1 x 120 W/cm Hg-bulb		

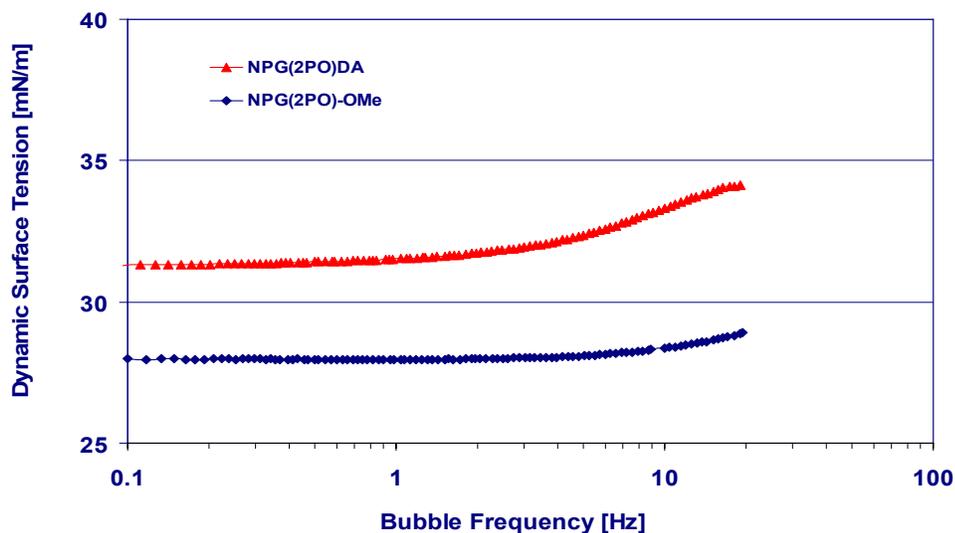
Two monomers NPG(2PO)DA and NPG(2PO)-OMe monoacrylate were used in identical amounts in the sprayable formulation (Table 3). The surface aspect of the two formulations is shown in Figure 4. The formulation containing the monomer NPG(2PO)-OMe monoacrylate with the lowest contact angle and surface

tension shows excellent coating coverage and surface smoothness. There is considerable “crawling” or withdrawal of coating of the formulation containing NPG(2PO)DA. The only structural difference between these monomers is a single methyl ether group.



**Figure 4** The surface aspect of UV cured coating on tin with NPG(2PO)DA and NPG(2PO) methylether acrylate

An analysis of dynamic surface tension of these two materials reveals significant differences (Figure 5). The graph shows that the initial surface tension of NPG(2PO)-OMe acrylate is lower than that for NPG(2PO)DA by



**Figure 5. Dynamic surface tension plot for NPG(2PO)DA and NPG(2PO) methylether acrylate**  
 Further the rise in dynamic surface tension over three orders of magnitude of bubble frequency is much smaller for NPG(2PO)-OMe acrylate versus NPG(2PO)DA. Bubble frequency is a proxy for rapidity of change of surfaces. This means that the methylether acrylate containing formulation is better able to maintain lower surface tension

and wet out the “oily” metal surface, as its undergoes very rapid and dynamic changes in its surface environment during the coating application process prior to UV curing of the coating.

**Case II Clear Topcoat on waterbased flexographic ink (PET film substrate**

In this formulation (Table 4) the requirement was for a clearcoat, with good reactivity, and low blocking resistance. Two formulations were used. The only difference was that formulation B lacked an acrylated polysiloxane block copolymer additive. As a class, silicone based surfactants are known to have among the lowest surface tension after fluorinated polyols. The no-overcoat requirement meant that we could use a silicone surfactant without worrying about intercoat adhesion issues encountered in multilayer UV coatings when the undercoat has silicone surface modifiers. Further, on curing an acrylated silicone is incorporated randomly through out the topcoat allowing for more control of slip properties and reduced blocking as evidenced from a lower slide angle and lower block resistance for the cured topcoat.

**Table 4: Clear OPV Formulation**

Material	A	B
Epoxy acrylate oligomer	78	78
Acrylated polysiloxane block copolymer S71UV	1	0
Benzophenone	8	8
Hydroxycyclohexylphenyl ketone	2	2
Triethanolamine	6	6
Amine acrylate	5	6
Total (wt.%)	100	100
Gloss (60°)	61	62
Slide Angle	14.2	27.8
Blocking Test (100psi, 24 h @ 60°C)	1	5
	1 = slight	5= severe

**Case III UV curable flexographic ink on Polyester film**

The requirements for this application were: Low and stable viscosity profile on the UV flexographic press, good pigment dispersion stability, good substrate wetting to PET and high gloss after cure. Non-homogenous systems like UV flexographic inks can present significant flow problems on a flexographic press. Typical symptoms such as high viscosity, poor ink flow across the roller train (the metering roll, fountain roll, the anilox and the impression cylinder), poor ink transfer to substrate and sub par color and print quality. These can be minimized using a) properly equipped roller train and b) UV flexographic inks with well chosen dispersants that wet out and stabilize the pigment.

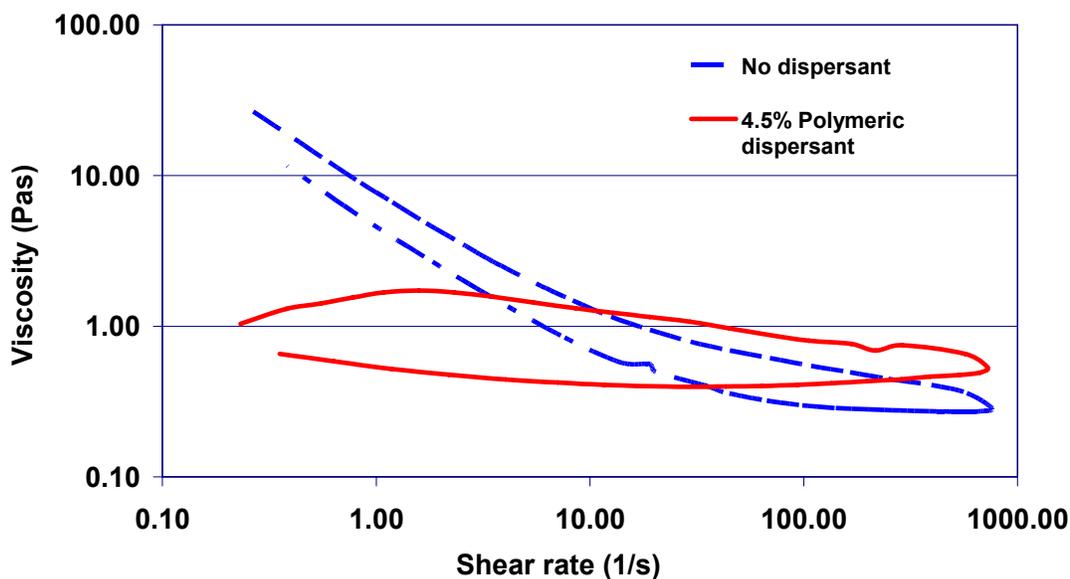
Table 5 shows a UV flexographic ink formulation for corona treated PET film. A control formulation did not contain the polymeric dispersant. Figure 6 shows Viscosity-Shear profile for these inks. From the figure its clear that the formulation without the dispersant exhibits a stronger shear thinning (Viscosity range of 8900-360 mPa.s

at  $1 \text{ s}^{-1}$  and  $1000 \text{ s}^{-1}$ ) versus the ink with the dispersant (Viscosity range of 1500-650 mPa.s at  $1 \text{ s}^{-1}$  and  $1000 \text{ s}^{-1}$ ). Both the “down-curve”(increasing shear) and the return “up-curve” (decreasing shear) for the dispersant containing UV ink exhibit manageable changes in viscosity all in the useful range for flexographic printing. No pigment settling was observed even after 6 months of storage.

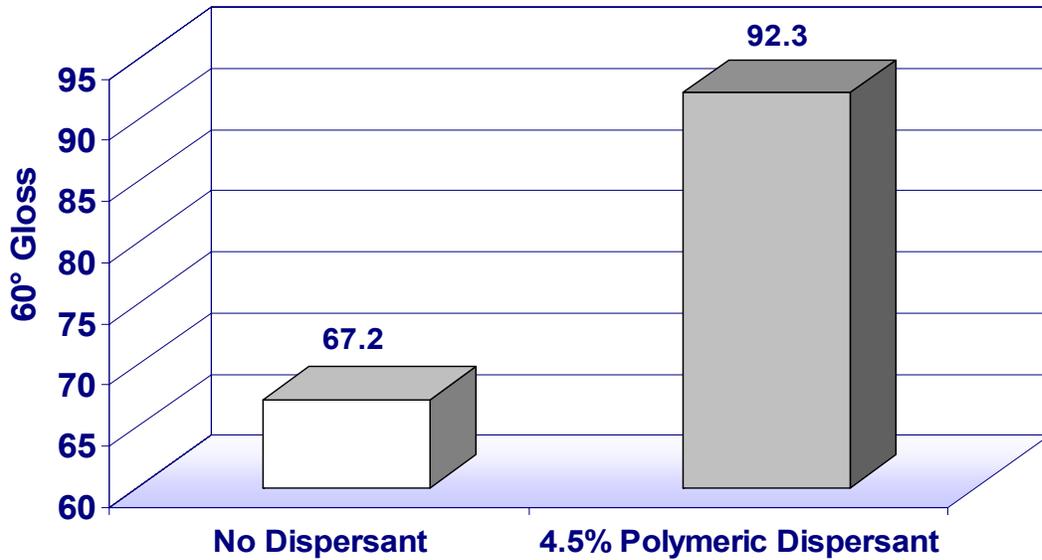
**Table 5: UV Curable flexographic ink formulation**

Product	Description	%
Bisphenol A (4EO)diacrylate	Reactive diluent	30
NPG(2PO)DA	Wetting and flow & leveling monomer	17
DPGDA	Reactive diluent	12
(EO)TMPTA	Reactive diluent	10
Red Pigment 219-0203	Pigment Red 57:1	16
Polyurethane SF73	Polymeric dispersant additive	4.5
UV 1	In-can stabilizer	0.5
Photoinitiator blend*	Photoinitiator blend	10
Total		100
Cure conditions : 4 $\mu\text{m}$ wet film thickness; speed 40 m/min; 1 x 120W/cm Hg bulb		
* Liquid Benzophenone 3.0 %    Morpholinophenylketone    3.0 % Isopropylthioxanthone 1.0 %    Ethyldimethylaminobenzoate 3.0 %		

In contrast to water based flexographic inks, UV curable inks are expected to have high gloss and possess better chemical resistance due to their highly cross linked nature. A dramatic 25 point improvement in cured ink gloss (Fig. 7) is also seen in the dispersant stabilized UV ink also implying the better pigment wet out by the binder in the dispersant containing ink.



**Figure 6: Viscosity vs. Shear strain rate plot for an UV flexographic ink with and without a polymeric dispersant.**



**Figure 7: 60° Gloss for UV flexographic ink with and without a polymeric dispersant.**

**Case IV: Matte Finish UV Wood Coating**

The requirement for this coating was with low gloss, matte aspect for a wood finish. The coating was applied using a roll coater and needed excellent de-airing prior to cure to prevent pin-holes and other defects that might produce reject parts due to poor aesthetic surface. Table 6 shows the formulation used in this application. The control formulation did not contain the polyurethane polymer dispersant.

**Table 6: Matt UV Coating Formulations**

Product	Description	%
PEA-1	Tetrafunctional polyester acrylate oligomer	80.5
Silica ED 30 <sup>1</sup>	Matting agent	12
Polyurethane P 61 <sup>2</sup>	Polyurethane dispersing additive	3.5
2-Hydroxy-2-methyl-1-phenyl propanone	Photoinitiator	4
Total		100
Cure conditions: 6-10µm wet film thickness ; speed 15 m/min ; 1x120 W/cm Hg bulb		

Figure 8 shows the rheology profile for the two formulations. The dispersant’s role in this case is two fold a) to displace air at the interface between the binder and the matting agent to help improve wet out of the inorganic

silica with the binder and b) keep the matting agent from settling while maintaining stable viscosity at different coating line speeds (i.e. different shear rates). Without the dispersant, the formulation is clearly more thixotropic and this clearly has the potential to cause poor flow and pin holes. Figure 9 shows the two formulations, after they were shaken in a paint shaker (high shear) for two minutes and then left alone (zero shear) for five minutes. The formulation without the dispersant clearly shows much higher air entrainment and no settling of the matting agent was observed. This shows the multifunctional role of the dispersant for pigment wet out, anti settling also acted as a de-airing agent.

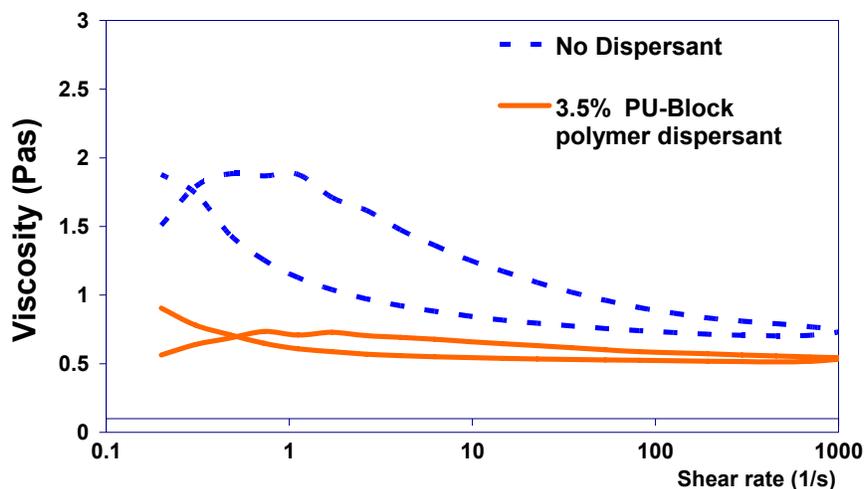


Figure 8: Viscosity vs. Shear strain rate for a matte UV wood coating with and without polymeric dispersant.

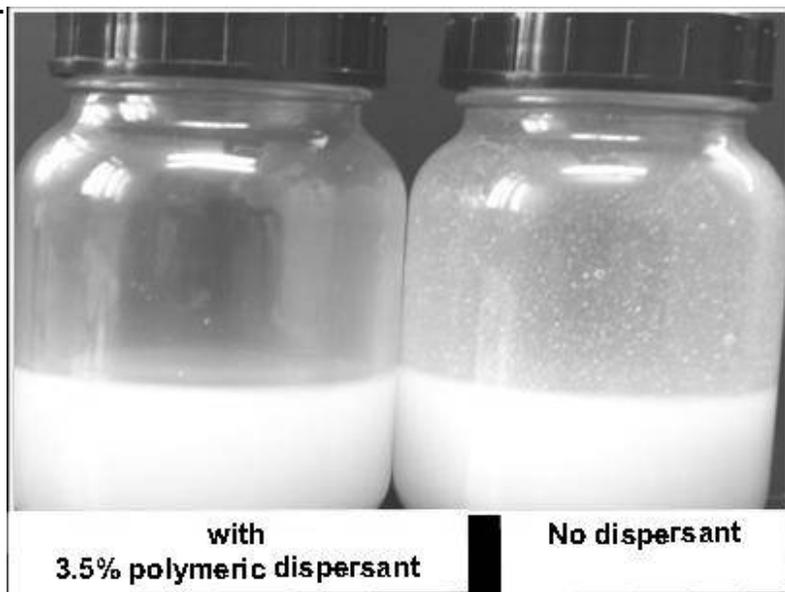


Figure 9: De-airing of a matte UV wood coating with and without polymeric dispersant.

## **Conclusions:**

The best choices to solve issues relating to slow and leveling challenges depend on the intended goal. If the goal is to get good wet out of low energy substrates, a combination of substrate surface treatment and the use of low viscosity UV curable, low surface tension monomers ex, neopentylglycol (2PO) monomethyl ether acrylate should help in coating wet out, flow and leveling. These monomers tend to have low substrate contact angles and are particularly useful in primers or undercoats. In contrast, for topcoats either block copolymer silicones or acrylated polysiloxane copolymers can be used to reduce coating surface tension. Better control of slip and block is expected from the acrylated silicones. To get optimum in storage, in-use and after cure application performance in pigmented (organic or inorganic) systems, well chosen polymeric (polyurethane) dispersants can produce dramatic changes in pigment wetting, dispersion stability and gloss control at low (3-5%) incorporation levels.

## **Acknowledgements:**

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## **References**

1. Radiation Curing of Polymeric Materials (1989), Edited by Charles E. Hoyle and J. F. Kinstle, Chapter 1, Photocurable Coatings, page 1-16
2. James E. Fleisher, Energy Curing for Plastics, November/December 2000 RADTECH REPORT, page 48-52
3. Kevin Josel, Process Conditions for UV Sealers for SMC Body Panels, November/December 2001 RADTECH REPORT, page 23-25
4. The Printing Ink Manual, Fifth Edition, Chapter 14, Rheology of Printing Inks, page 766-775, Edited by R. H. Leach and R. J. Pierce.