

New Additive Chemistry for Improved Pigment Suspension Control in Non-Aqueous UV Cured High Performance Coatings

Scott Murray, William A. Reynolds & Detlef van Peij, Elementis Specialties, Inc.

With steady growth of radiation cured systems for high performance industrial coatings, new challenges constantly arise that require innovative solutions. Obtaining desired sag control and pigment suspension often requires sacrificing coating performance for acceptable spray or roll coat viscosity by varying oligomer to monomer ratios. Additives for the traditional coatings market may not provide acceptable solutions to many UV formulation problems therefore the need to offer new alternatives arise.

This paper will provide insight into a new polyester based rheology modifying additive chemistry, to help eliminate some common rheological problems and optimize pigmented UV coatings. Coatings formulators will get a full picture regarding a new developmental composition, its base chemistry and incorporation procedures to enhance coating properties and performance.

When the end user or applicator opens the container, the last thing they would like to experience is finding the pigment hard settled at the bottom which brings the products storage stability into account. From a product stability standpoint the issue of pigment settling is not simply a matter of aesthetics. Performance too is an issue. When pigments hard settle they tend to pack to the point where they become dry (see Figure 1). The dispersants and solvating fluids which initially dispersed the pigments into suspension have been forced off of the pigment particles. One symptom of this phenomenon is a loss of the fineness of grind after attempting to reincorporate the settled cake. In most cases the pigments can not be reincorporated back into suspension. These dry particles are applied with the coating onto the substrate. They will tend to form surface defects and inhibit the coating from forming a uniform film. Premature coating failure is likely along with poor appearance.

To a degree these same forces involved in pigment settling affect the sag resistance and leveling of coatings. To better understand these interactions and forces and how to mitigate them, a basic knowledge of rheology and how to measure it is required.

Figure 1 Settled Dry Cake on a spatula



Basic Practical Rheology

When we think of the word Viscosity we relate it to how “thick” something is when it is mixed or shaken. Viscosity is the resistance of a material to flow when we apply a force (or stress) such as mixing.¹ Shear stress (τ , pronounced “tau”) is an external force (mixing, shaking).² Shear rate ($\dot{\gamma}$, pronounced “gamma dot”) measured in reciprocal seconds (s^{-1}) is how fast we move the liquid layers in a material of given thickness when we stir with an applied force.³ Shear rate is a velocity gradient to liquid thickness relationship. Viscosity (η , pronounced “eta”) is then the ratio of shear stress to shear rate and can be measured and reported as a Pascal second (Pa·s) or in Poise where 1 Pa·s = 10 Poise = 1000 centi-Poise (cP) or 1000 mPa·s.

Viscosity measurement is relative to the shear rate at which it is tested by use of various viscometers that have become common to us. A Stormer viscometer will measure viscosity at one point in the medium shear rate range equivalent to normal stirring or hand mixing, $\sim 200 s^{-1}$. Brookfield viscometers can measure multiple point shear rates using different spindle sizes and rotational speeds to determine viscosities in the range of $1.0 - 100 s^{-1}$. Because of the expanded measurement ranges in shear rate, albeit a small portion of the overall rheology profile, a Brookfield will help provide a better picture of the coatings flow. Pigment settling, leveling and resistance to sag cannot be measured efficiently with these methods as they can only be measured at ultra-low shear rates. Therefore, a rotor stator type rheometer which can provide more precise measurements of ultra-low, low, medium and high shear rates is the preferred method when studying the rheology and flow of coatings.

Knowing the viscosity at the different shear rates during production, application, transportation and storage can be invaluable. By using a rheometer with a series of viscosity measurements at these shear rates, a viscosity profile or flow curve can be generated for a coating. Such a profile will provide reliable information as to how a coating will perform at a given point of its life prior to application and cure.

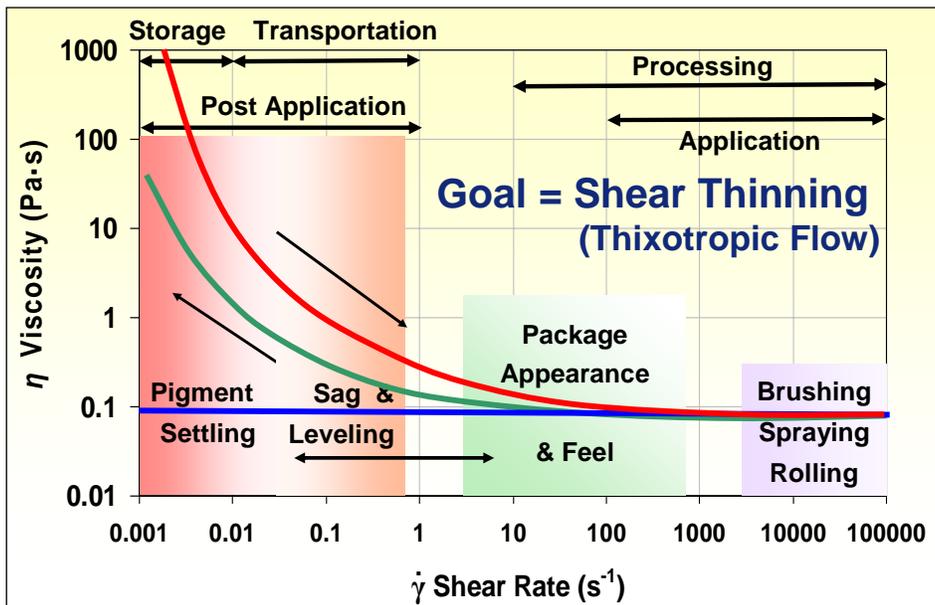
Types of Flow

When the viscosity is measured at increasing or decreasing shear rates, the result is a flow diagram or viscosity profile which can be compared against that of other coatings to help judge their overall performance. A Newtonian flow profile (see Figure 2, lowest flat line) maintains constant viscosity regardless of the applied shear rate. This type of flow is typical of common materials such as honey, solvent and resins but undesirable in most finished coatings.⁴

The goal of many formulators is to provide a coating with a Pseudo-plastic or Thixotropic flow profile (see Figure 2, top (down arrow) line – initial; lower (up arrow) line - recovery) that is ‘shear thinning’ to some degree.

In a shear thinning system the cohesive bonds or attractive forces between molecules and particles are broken as shear rate increases resulting in a lower viscosity. Once the shear is removed, a Pseudo-plastic system will recover immediately (e.g. latex emulsion) while a Thixotropic system will recover with time (e.g. oil based dispersion paint). The area between the initial viscosity curve and the recovery curve, the hysteresis loop, is a measure of the systems thixotropy.

Figure 2 Thixotropic & Newtonian Rheology Profiles with Related Coating Properties



Pigment suspension is determined by how well the coating resists the pigments tendency to settle through the coating to the bottom of the container when affected by shear stresses, in the ultra low shear rate ranges, exerted by gravity, post-production packaging and transportation.⁵ Sag resistance and leveling are also influenced and controlled in these low shear regions.

As a shear thinning system recovers its low shear viscosity after application, yield values (Yield value is the minimum shear stress needed to induce flow (measured in Newton/m² or Pascal's (Pa)) must be high enough to exceed the effect of gravity which causes settling in the paint or the applied coating to sag.

For a shear thinning system, fast recovery equals good sag control but causes poor leveling as evidenced by 'brush strokes'. If the time to recover is too long, then the coating will sag. The need for a coatings system to exhibit a proper balance between flow and leveling becomes readily apparent as does the need for rheology modification to obtain these properties.

Formulation Concerns and Limitations

When the form, function and cost of a coating system have been determined between the manufacturer, customer and applicator, the balancing act for the formulator begins.

It is a common practice to alter a coatings viscosity until it has achieved the desired application viscosity "spray viscosity" or good "in-can" or "feel". It is beneficial for the coating to be at the application viscosity when the customer opens the can to retard the desire to improperly thin the coating and cause other application difficulties. However, as previously mentioned, if a low viscosity is prevalent in the ultra low shear range, pigment suspension and sag control suffer. Obtaining a suitable application viscosity also presents additional concerns for the formulator when the coating contains little or no solvent. The oligomer to monomer ratio in many cases is the first area subject to adjustment. Reduction of a viscous high molecular weight oligomer with a monomer may diminish desired properties over the reality of needing a lower viscosity, lower average molecular weight oligomer/monomer blend. This may adversely affect the performance of the coating and simultaneously hinder pigment suspension as the nature of the flow will lean toward Newtonian.

This balancing act also affects the types of pigment used and their loading. If a low viscosity system is desired, using pigments and extenders with a low oil absorption such as Calcium Carbonate or Barium Sulfate (Barytes) must be used. Benefits include improved sanding capabilities, hiding power and a lower overall cost. One drawback in the use of these pigments is their high density combined with their low oil absorption properties which greatly increases their tendency to hard-pack settle. Thus, their use is limited. Silica's or other higher oil absorption pigments may be needed to achieve the desired gloss or hiding which typically drive up the viscosity as well as raw material cost. While silica's can improve pigment settling to a degree, many times their handling during manufacture becomes an issue.

The result of manipulating the viscosity by using these methods will result in a primarily Newtonian flow that remains still be plagued with the common problems – lack of rheology control, pigment settling and poor sag resistance. Only by the use of efficient rheology modifiers can practical solutions be found.

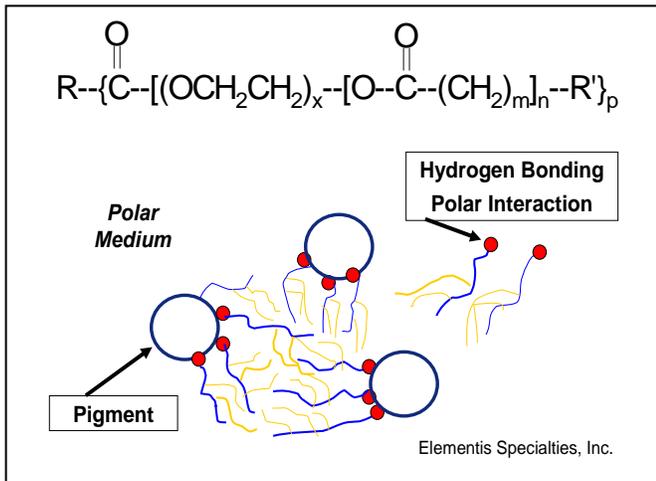
Formulation Solutions and Additional Benefits

The availability of rheology additives to the energy cured coatings market has been rather limited. Solvent content, incompatibilities and products which provide too great an increase in the application viscosity have failed to bridge the gap between necessity and practicality. A new polyester based rheology modifier chemistry has been developed in response to offer a practical solution to these vexing problems. This new rheological additive was designed as a 100% non volatile, easily incorporated, liquid thixotrope for use in pigmented radiation cured and conventional high solids coatings. It can effectively replace conventional thixotropes or be used as a synergist in combination with other rheological additives. Rheology control is now possible as it imparts high viscosity and good yield value in the ultra low shear rate regions with a highly desirable shear thinning effect and excellent recovery to establish a Thixotropic flow profile. A lower application viscosity than traditional thixotropes is now realized while maintaining the rheological performance properties necessary to control sag and pigment suspension in the final coating formulation.

Functionality and Mechanism

This additive functions by use of an associative mechanism with pigments or extenders. It is specifically designed to provide superior rheological characteristics based on its two-part structure (see Figure 3). This structure includes an anchoring functional group attached to a solvatable chain and hydroxyl groups. Multiple anchoring groups associate with various particle surfaces. The structure resulting from the use of the hydroxyl groups is an artifact of polar bonding such as hydrogen bonding. This same phenomenon is observed between polar species with other components present in the coating formulation. This provides a three dimensional structure which increases the molecular volume and chain entanglement, subsequently increasing the viscosity in the ultra-low shear ranges.

Figure 3 Mechanism and Chemistry



These structures are weakly associated with their attractive forces and are easily disrupted under applied shear during mixing, spraying, etc. This results in a desirable shear thinning viscosity reduction for easy handling and application properties while providing good pigment suspension during storage.

Figure 4 Rheology Modifier Incorporation

Additive Use / Order of Addition

When formulating with this associative thixotrope, order of addition is important. This additive requires intimate contact with dispersed particulates and should always be added after the pigment. Figure 4 relates the best possible scenario for obtaining the desired results. Temperature ranges will vary due to the overall solvency and shear imparted into the system during coating manufacture.

1. Oligomer/Monomer Combination, add:
2. Pigments/Colorants & Dispersants
Mix until Homogenous, then add:
3. Polyester Rheological Modifier
High Speed Disperse @ 49 -52°C for 15- 20 minutes or until desired Fineness of Grind
4. Letdown – Able to Pack out Hot

Supporting Data

Two case studies have been provided to show the efficiency of the rheology modifier.

Case Study 1 – Wood Primer/Sealer

The first is a 100% solids UV curable Primer/Sealer Wood coating with a Polyester/Polyether Acrylate Oligomer blend, various common monomers and Talc and Barium Sulfate as fillers. The application is designed for room temperature HVLP spray application; the viscosity measured using a # 4 FORD cup at 25°C.

The following rheology profiles (see Figure 5) exhibit the changes produced by the addition of this thixotrope at 0.6% by weight opposed to using none. The flow profile for the blank and the sample with the rheology modifier show a similar response to shear. However, further examination reveals that the sample with the polyester rheology modifier provides a higher ultra low-shear viscosity and the development of more

thixotropy (as denoted by the area inside the hysteresis loop) than does the blank. The blank has hard pigment settling and no measurable resistance to sagging (see Table 1) which relates to the lack of ultra low shear viscosity and how it will impact a coatings performance. The sample with the polyester rheology modifier is very efficient in eliminating hard-packed settling with a slight improvement in sag resistance without a significant effect on viscosity.

Table 1 Wood Primer Sealer Test Data

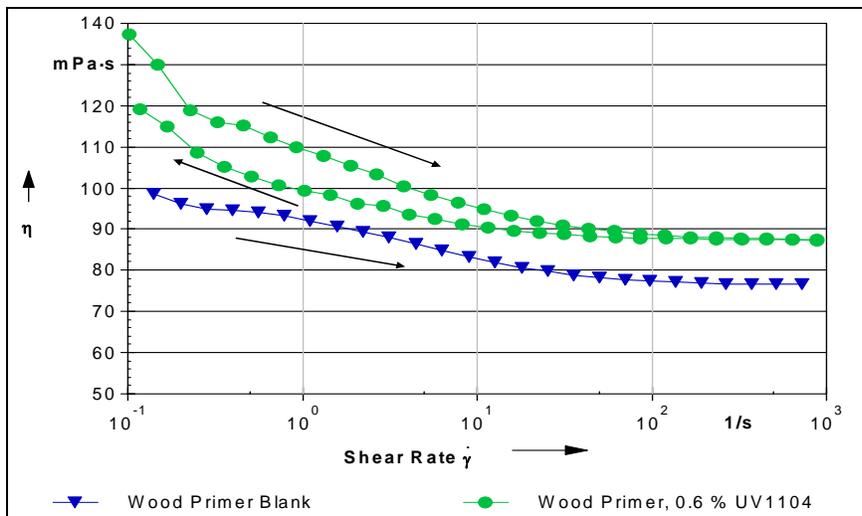
Sample Loading level	Blank	0.6 % Polyester Rheology Modifier	Benefits
<i>Initial Overnight</i>			
Fineness [μm] Hegman Reading	15 6.75 C*	22 6.25 A	*Blank – Heavy Scatters
Viscosity #4 Ford cup [s]	23	25	Slight Impact
Sag resistance [μm]	5	13	Marked Improvement
# Settling ASTM D 829	4 acceptable	7 good	Significant Improvement
<i>Oven Aged 7 days at 49°C</i>			
Fineness [μm] Hegman Reading	22 6.25 BC*	22 6.25 A	Stable
Viscosity #4 Ford cup [s]	23	25	No Growth
Sag Resistance [μm]	5	13	No loss on Aging
# Settling ASTM D 829	1 hard pack settling	6 good	Superior Storage Stability

Settling (1=worst; 10=best)

Also notice the improved cleanliness in the fineness of grind and the stable viscosity upon oven aging. The sample using the polyester rheology modifier shows no change in these values as the additive has a stabilizing effect on the pigments in the coating. Shelf life and performance have been markedly improved by use of

this product. As previously discussed using fillers such as Barytes can improve the coatings performance during sanding operations and reduce the raw materials cost while having a low impact on the viscosity because of its low oil absorption. Unfortunately the low oil absorption increases the pigments settling tendency as evidenced in the blank sample. It was the goal of this evaluation to have coatings at a “spray viscosity” with a variety of dense pigments to show the usefulness of the Rheological additive and how it prevents hard pack settling. This has been accomplished.

Figure 5 Wood Primer/Sealer Rheology Profiles



Case Study 2 – White Plastic Topcoat

The second case study is a 100% solids UV curable white topcoat for plastic substrates. The Oligomer is a Polyester Acrylate. Other constituents include an alkoxyated triacrylate adhesion promoter, common monomers and Titanium Dioxide pigment. This system was designed for application using a roll coater, heated spray or as a reducible concentrate.

Table 2 Plastic Coatings Test Data

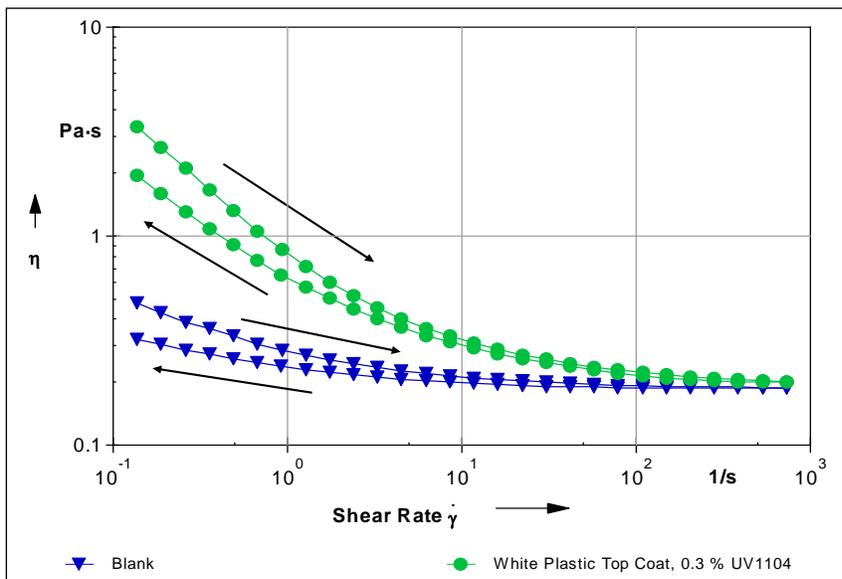
Sample Loading level [%]	Blank	0.3 % Polyester Rheology Modifier	Benefits
<i>Initial Overnight</i>			
Fineness [μm]	18	15	
Hegman Reading	6.5 B	6.75 A	
Viscosity #4 Ford cup [s]	52	54	Low Impact
Sag resistance [μm]	38	51	Improved
* Settling ASTM D 829	8 very good	10 excellent	Blank is Good Initially
<i>Oven Aged 7 days at 49°C</i>			
Fineness [μm]	18	18	Stable
Hegman Reading	6.5 B	6.5 A	
Viscosity #4 Ford cup [s]	46	52	Stability
Sag Resistance [μm]	38	51	No Loss on Aging
* Settling ASTM D 829	3 hard settling	8 very good	Superior Storage Stability

* Settling (1=worst; 10=best)

Performance issues regarding the coating included pigment settling and unstable viscosity upon oven aging. Aesthetically, the coating had exhibited orange peeling as a surface defect (see Table 2). When the polyester rheology modifier was incorporated, the pigment settling and viscosity stability of the sample was considerably improved

without an unacceptable increase in viscosity. Surface defects were eliminated and sag resistance has also increased. The blank sample exhibits a far less shear thinning flow profile (see Figure 6). Increases in the low shear viscosities as evidenced by the rheological profiles provide a valid illustration that many issues regarding product stability and appearance will benefit when the proper thixotropic additive is utilized.

Figure 6 Plastic Topcoat Rheology Profiles



When using the polyester rheology modifier to control the viscosity recovery (shown by the back (lower curve)) we can attain the proper balance between sag control and leveling needed to prevent surface defects while maintaining the maximum sag control. This case study is regarded as a success as well.

Conclusions

A novel polyester rheological modifier has been developed in response to the needs of the energy cured coatings industry to assist the formulator in rheology control. This product provides lower viscosity than traditional thixotropes while maintaining rheological performance properties necessary to improve sag and pigment suspension in the final coating. It will help a formulator to meet and exceed performance and storage stability expectations over current methods. Additional potential benefits include improved performance, appearance, and cost reduction in raw materials and in coating application.

References

- ¹ "Rheology Handbook-A Practical Guide to Rheological Additives"; Elementis Specialties, Inc.; pages 1-2
- ² "The Rheology Handbook: For users of rotational and oscillation rheometers"; Metzger, T. G.; Vincentz Verlag; page 17
- ³ "The Rheology Handbook: For users of rotational and oscillation rheometers"; Metzger, T. G.; Vincentz Verlag; page 17
- ⁴ "Rheology Handbook-A Practical Guide to Rheological Additives"; Elementis Specialties, Inc.; pages 1-2
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