

# MATTING ENERGY-CURABLE COATINGS THROUGH NOVEL DISPERSANT TECHNOLOGY

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## **ABSTRACT**

Energy-curable coatings continue to grow and provide multiple benefits to the wood coatings industry. The ability to decrease gloss levels within the traditional 100% solids or solvent reduced systems has always been a challenge. With this in mind, novel dispersants are being developed to allow the formulator the ability to utilize common silica-based matting agents to achieve extremely low gloss levels. Not only is it possible to achieve low gloss levels, but these novel dispersants perform at a rheological profile which is commercially acceptable. In this study, novel dispersant technology is explored to provide formulation guidance on how to achieve low gloss or matte systems, while maintaining a workable viscosity using traditional matting agents.

## Introduction

Matting energy-curable systems continues to be a concern for formulators within the wood coatings industry. The matting of the system requires the appropriate matting agent selection in accordance with the desired end-use properties. The negative rheological effects (i.e. high viscosities) encountered by the introduction of a silicon dioxide matting agent makes formulation extremely difficult.

In response, matting agents are often modified to promote “compatibility” within a given system. Compatibility is typically increased via after-treatments like waxes or polymers. Wax modifications tend to increase a matting agent’s suspension behavior, thereby improving both its overall stability and its ability to be dispersed within a given system. Polymer treatments, on the other hand, aid in the encapsulation of matting agent particles within an active network and thereby minimize the coating’s thixotropic tendencies.

Though both surface modifications drastically improve the rheological properties of matte coatings, novel dispersant technology can also be applied to aid formulators in achieving extremely low gloss levels, while maintaining a commercially acceptable viscosity profile. An evaluation of common silica-based matting agents, including those mentioned above has been performed in conjunction with novel dispersant technology within a 100% energy-curable system to demonstrate the rheological effects of dispersants on silica-based matting agents.

## Definition and Traits of Gloss/Matte Coatings

The gloss of an ink/coating is a measure of its ability to reflect incident light and depends, to a large extent, on whether or not the ink/coating forms a smooth film on the surface of the substrate and masks any irregularities<sup>5</sup>. In the case of matte coatings, optimizing irregularities within the coating is vital to obtaining a successful matte effect. By disrupting the coating surface, incident light cannot be reflected back to the observer’s focal point, but is scattered both within the coating and away from the coating surface.

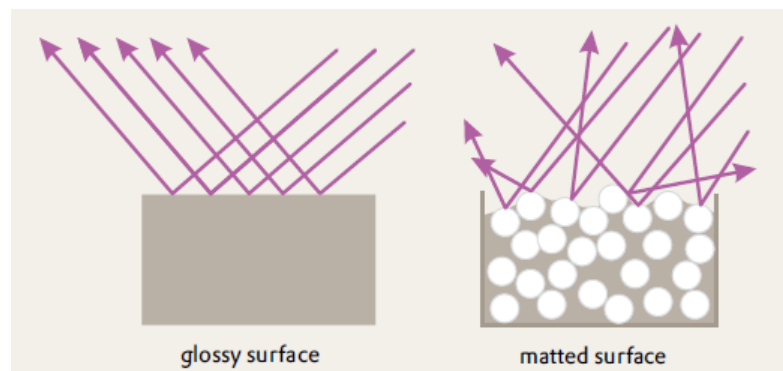


Figure A: Mechanism of gloss reduction<sup>2,3</sup>

Unlike solvent and water-based coatings which rely on evaporation of the coating system to decrease and “shrink” the film to create a rough surface, energy-curable or 100% solids systems do not benefit from this phenomenon. Thus, matting energy-curable wood coating systems becomes a daunting task, dependent upon matting agent choice and the ability to suspend and disperse these particles within the system. By uniformly suspending and dispersing particles, the surface roughness of the energy-

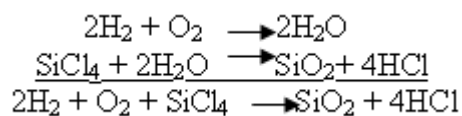
curable coating is increased, respectively decreasing the gloss value. The resultant coating is considered matte and is typically measured using a reflectometer/glossmeter with the 60° angle being well-regarded as the standard for the measurement of matte coating surfaces.

Within this piece of literature, coatings which are considered matte are those coatings which offer a gloss value less than 20.0 when measured by the 60° angle of a reflectometer/glossmeter. In addition, coatings exemplifying a viscosity of 2000-6000cps are considered commercially acceptable.

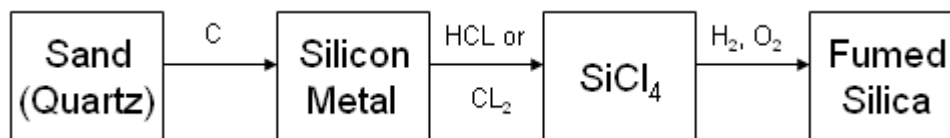
## Matting Agent Technologies

### Fumed (Thermal) Silica

The preparation of fumed silica is performed by a vapor process. Hydrolysis of silicon tetrachloride is accomplished in a flame of hydrogen and oxygen at a temperature of 1600-1800°C (Equation 1):



Equation 1: Hydrolysis of silicon tetrachloride<sup>1,7</sup>



Flowchart 1: Manufacturing process for fumed silica<sup>7</sup>

Key characteristics of fumed silicas, such as particle size and surface area, are controlled by varying reactants within the reaction. Furthermore, fumed silicas tend to be the most expensive form of silica preparation but are often used due to high purity, unique surface chemistry, and small particle size. Despite these favorable characteristics, untreated fumed silicas are generally difficult to disperse and demonstrate unfavorable suspension characteristics<sup>2</sup>.

In this study, Matting Agent #1 has been characterized as fumed (thermal) silica, consisting of average agglomerate particle sizes of approximately 10µm which have not been modified with hydrophilic, hydrophobic, or metal oxide surface treatments. Therefore, the effects of novel dispersing additives will be especially interesting given that dispersing and stabilization characteristics are solely a function of the interaction of untreated fumed silica and dispersant. Thus, rheological adjustments will not be influenced by designed surface modifications.

## Precipitated Silicas

While there are many methods to preparing precipitated silica, with variations from process to process, two common methods for the production of precipitated silica are illustrated below (Equation 2):



Or



Equation 2: Production of precipitated silica<sup>8</sup>

Similar to fumed silicas, precipitated silica characteristics are distinguished by particle size, surface area, and oil absorption. Silicas tend to follow typical particle interaction rules and are composed of primary/ultimate particles, secondary/aggregate particles, and tertiary/agglomerate particles. Silica stability is dependent upon the ability to stabilize and suspend aggregates, as agglomerations do not withstand the shear forces associated with the proper preparation of matte coatings and ultimate particles are generally viewed as only relevant in theory<sup>8</sup>.

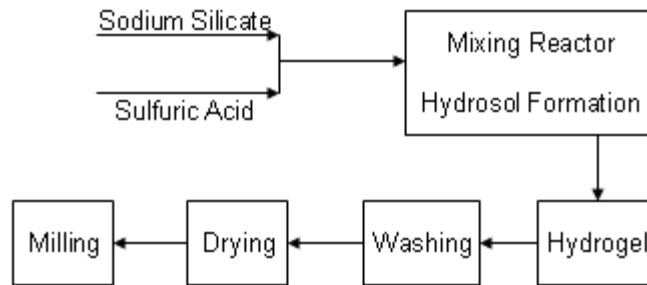
Stability of precipitated silicas can also be improved with the application of surface preparations. These preparations aid in the suspension behavior and/or wetting characteristics of the silica particles. Matting Agent #2 is an all-purpose matting agent which has an average agglomerate particle size of 6 $\mu\text{m}$  and has been treated with an organic wax for improvement of its suspension behavior within a coating's system. Matting Agent #3 is a fine-grained matting agent with an average agglomerate particle size of 5 $\mu\text{m}$  and has been polymer treated to aid with both wetting and particle/liquid medium stabilization.

## Silica Gels

Like precipitated silicas, silica gels are also prepared by a liquid manufacturing process. Silica gels are prepared by the acidification of an alkali metal silicate with an acid under controlled conditions (Equation 3). By controlling gelation conditions, and both the washing and drying steps, the properties of silica gels can be modified to prepare an infinite number of silica gels<sup>9</sup>. With specific control of the drying phase, silica gels, called xerogels and aerogels, can be prepared. Xerogels are highly porous, high-density, low pore volume materials produced by drying the hydrogel very slowly. Inversely, aerogels are low-density, high pore volume, low shrinkage silica gels prepared by a rapid drying process.



Equation 3: Acidification of alkali metal silicate<sup>9</sup>



Flowchart 2: Silica gel manufacturing process<sup>9</sup>

Though silica gels are the oldest and generally more expensive than the precipitated silica technologies, these materials are still widely used in the coatings industry as matting agents. Matting Agent #4, Matting Agent #5, and Matting Agent #6 evaluated within this composition are all members of the silica gel preparation method. Matting Agent #4 is organically treated, has an aggregate particle size of 5.9-7.6 $\mu\text{m}$  and a pore volume of 1.8ml/g. Matting Agent #5 and Matting Agent #6 are of the aerogel silica gel preparation and range in particle size from 2-24 $\mu\text{m}$ . While both Matting Agent #5 and #6 are very similar in terms of physical characteristics, the raw materials used for their manufacture differ significantly. Due to this difference, Matting Agent #6 has a greater potential to breakdown under shear, making it a better choice for use in energy-curable matte coatings.

## Dispersant Technology

Novel dispersing technology influences many characteristics within a wood coating. Color strength, hiding power, flocculation, flooding and floating, gloss and rheology are the key characteristics influenced by dispersant technology<sup>6</sup>. Gloss and rheology are the focus of this evaluation, but in order to understand the influence of dispersant technology, a brief theoretical background is both important and necessary.

Novel dispersant technology influences wetting, dispersion, and stabilization of particles within the manufacturing process:

Wetting of particles can be defined as the replacement of air trapped between particles by a liquid medium. This will occur if the liquid phase is lower in surface tension than the particles being wetted. Due to this phenomenon, novel dispersants are adsorbed onto the particle surface, in this case matting agent surfaces, encapsulate the particles, reduce interactions, and thereby assist in the decrease of the coating's viscosity.

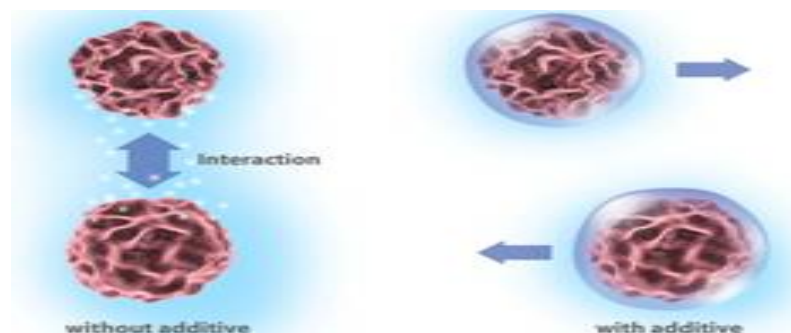


Figure B: Dispersant/Particle interaction<sup>4</sup>

The dispersion process can continue as the particles have been wet out with dispersant technologies. Due to the decreased interactions of particles, as previously mentioned, the viscosity of a given coating system is reduced, allowing the formulator the ability to incorporate higher particle concentrations (i.e. matting agent), which will aid the formulator in achieving the targeted gloss value for matte coatings. Additionally, it can be said that the work needed to perform the dispersion process is related to the surface area of the particles involved:

$$dW = \gamma * dA$$

where

W = interfacial surface energy  
 $\gamma$  = surface tension  
A = interface area

Equation 4: Relationship of work and surface area<sup>4</sup>

Equation 4 shows that for an increase in area, dA, of the surface during dispersion - by breaking up agglomerates - an energy, dW, proportional to the surface tension,  $\gamma$ , is necessary<sup>6</sup>. Novel dispersants have an effect on wetting by contributing mostly to a decrease in surface energy. Furthermore, for a change in surface area in the presence of a novel dispersant, less dispersion energy or work is required to properly disperse particles within a coating medium.

The stabilization potential of novel dispersant technology is dependent on the coating system as well as the choice of dispersing additive. Typically in water-based systems, electrostatic stabilization is the most prominent mode of stabilization. Unfortunately, this stabilization technique is not effective in solvent-based and energy-curable coatings. Steric stabilization or electrosteric stabilization methods, dependent on the chemical structure of novel dispersant additives, are utilized within energy-curable coatings. Steric stabilization is the result of dispersant additives whose chemical groups have an affinity for the particles being dispersed (i.e. matting agents). By this system, novel dispersants anchor themselves to the particles surface and prevent the re-agglomeration of aggregates by restricting mobility due to side chain interactions.

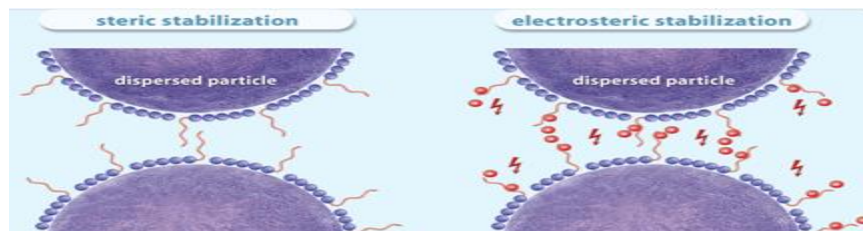


Figure C: Stabilization mechanisms<sup>4,6</sup>

Novel dispersing additives which provide an electrosteric stabilization capacity simply combine the techniques of electrostatic and steric stabilization. The combination of these modes allow for complex and diverse dispersing additives which control the aforementioned issues.

## Experimental Details

- Draw-down was applied to a black Leneta chart, form BK.
- UV-drying was performed using a Fusion UV Systems F300S at 60fpm with average intensity of  $1.3\text{W}/\text{cm}^2$  and dosing of  $0.15\text{J}/\text{cm}^2$ .
- Viscosity profile executed on a Haake RheoStress 1 at varying shear rates ( $m\text{Pas}=\text{cps}$ ).
- Gloss readings obtained from BYK Gardner Micro Tri-Gloss Reflectometer

## Test Formulas

To minimize the variability within the tested formulations, the monomer/oligomer ratios remained constant, eliminating any variations associated with the volume shrinkage of the tested medium. Additionally, the photoinitiator concentration remained equal to mitigate the influence cure-speed and crosslink density would have on reflectometer values. The testing parameters focused solely on silica particles and the interaction of a novel dispersant with those particles within the energy-curable formulations below:

<b>Formula #1</b>	<b>Blank</b>	<b>w/ additive</b>
Aliphatic Urethane Triacrylate	26	26
Polyester Tetra-acrylate	9.3	9.3
Dipropylene Glycol Diacrylate	37.7	37.7
UV Stabilizer	1	1
Benzophenone	3.4	3.4
HMPP	2.3	2.3
Novel Dispersant		6
Matting Agent #1	11.3 of 14.3	14.3

<b>Formula #2</b>	<b>Blank</b>	<b>w/ additive</b>
Aliphatic Urethane Triacrylate	28	28
Polyester Tetra-acrylate	9.3	9.3
Dipropylene Glycol Diacrylate	38.5	38.5
UV Stabilizer	1	1
Benzophenone	3.4	3.4
HMPP	2.3	2.3
Novel Dispersant		1.5
Matting Agent #2	16	16

<b>Formula #3</b>	<b>Blank</b>	<b>w/ additive</b>
Aliphatic Urethane Triacrylate	28.8	28.8
Polyester Tetra-acrylate	9.3	9.3
Dipropylene Glycol Diacrylate	38.2	38.2
UV Stabilizer	1	1
Benzophenone	3.4	3.4
HMPP	2.3	2.3
Novel Dispersant		1
Matting Agent #3	16	16

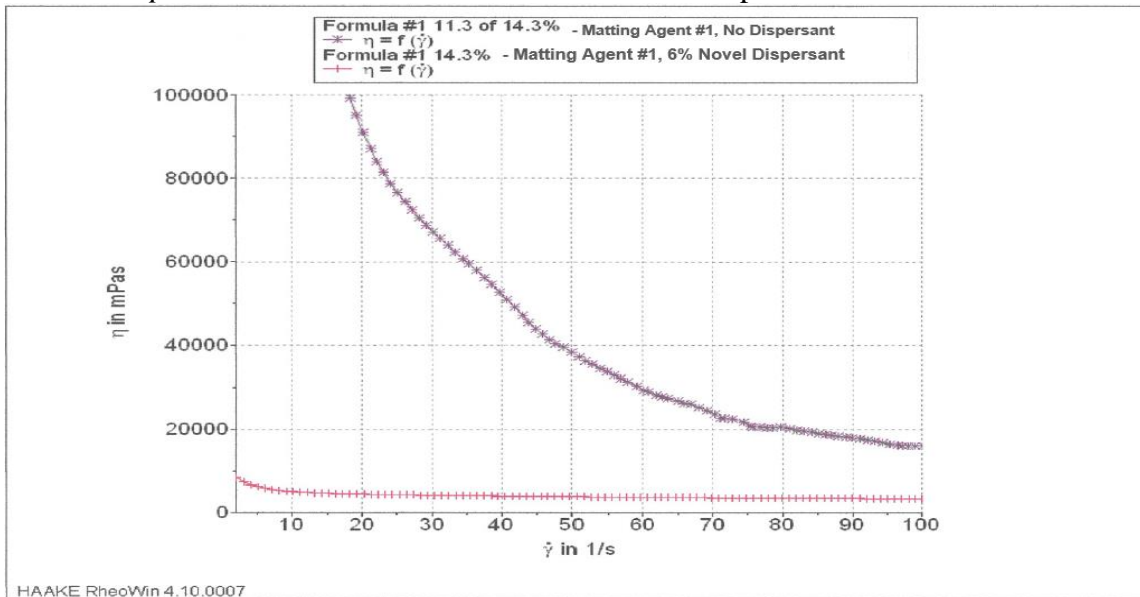
<b>Formula #4</b>	<b>Blank</b>	<b>w/ additive</b>
Aliphatic Urethane Triacrylate	29.5	29.5
Polyester Tetra-acrylate	9.3	9.3
Dipropylene Glycol Diacrylate	39.3	39.3
UV Stabilizer	1	1
Benzophenone	3.4	3.4
HMPP	2.3	2.3
Novel Dispersant		0.5
Matting Agent #4	14	14

<b>Formula #5</b>	<b>Blank</b>	<b>w/ additive</b>	<b>w/ add. monomer</b>
Aliphatic Urethane Triacrylate	34	34	34
Polyester Tetra-acrylate	9.3	9.3	9.3
Dipropylene Glycol Diacrylate	43	43	45
UV Stabilizer	1	1	1
Benzophenone	3.4	3.4	3.4
HMPP	2.3	2.3	2.3
Novel Dispersant		2	
Matting Agent #5	5	5	5

<b>Formula #6</b>	<b>Blank</b>	<b>w/ additive</b>	<b>w/ add. monomer</b>
Aliphatic Urethane Triacrylate	34	34	34
Polyester Tetra-acrylate	9.3	9.3	9.3
Dipropylene Glycol Diacrylate	44	44	45
UV Stabilizer	1	1	1
Benzophenone	3.4	3.4	3.4
HMPP	2.3	2.3	2.3
Novel Dispersant		1	
Matting Agent #6	5	5	5

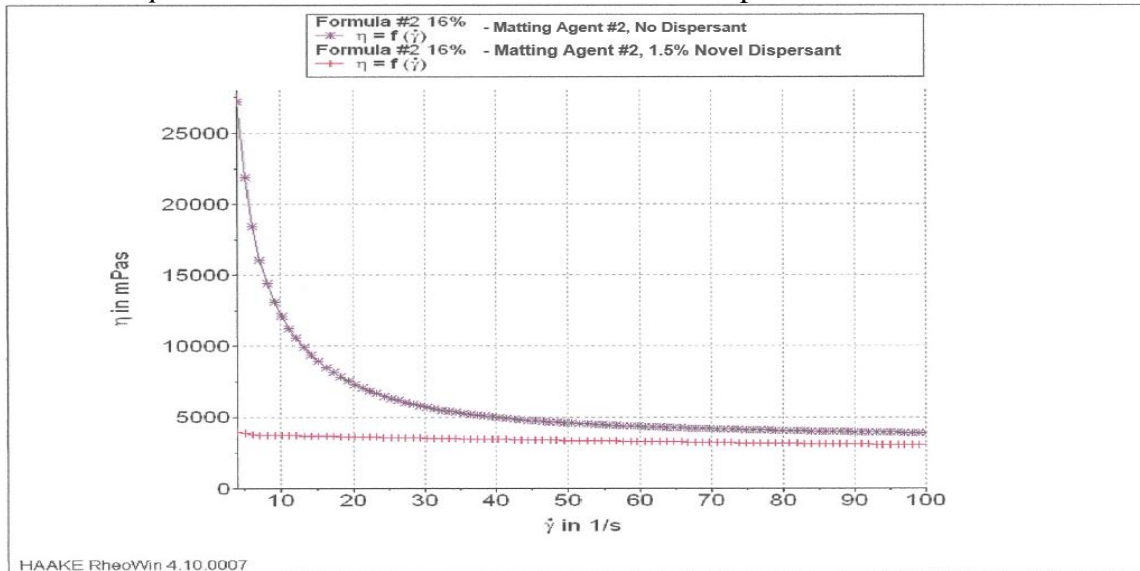
# Graphical Results

Graph #1: Formula #1 with and without novel dispersant additive



<b>Formula #1 Results</b>	<b>Blank</b>	<b>w/ additive</b>
Viscosity (2.0sec <sup>-1</sup> ), cps	561,700	8,465
Viscosity (100sec <sup>-1</sup> ), cps	15,960	3,295
Reflectometer Value (60° Angle)	-	37

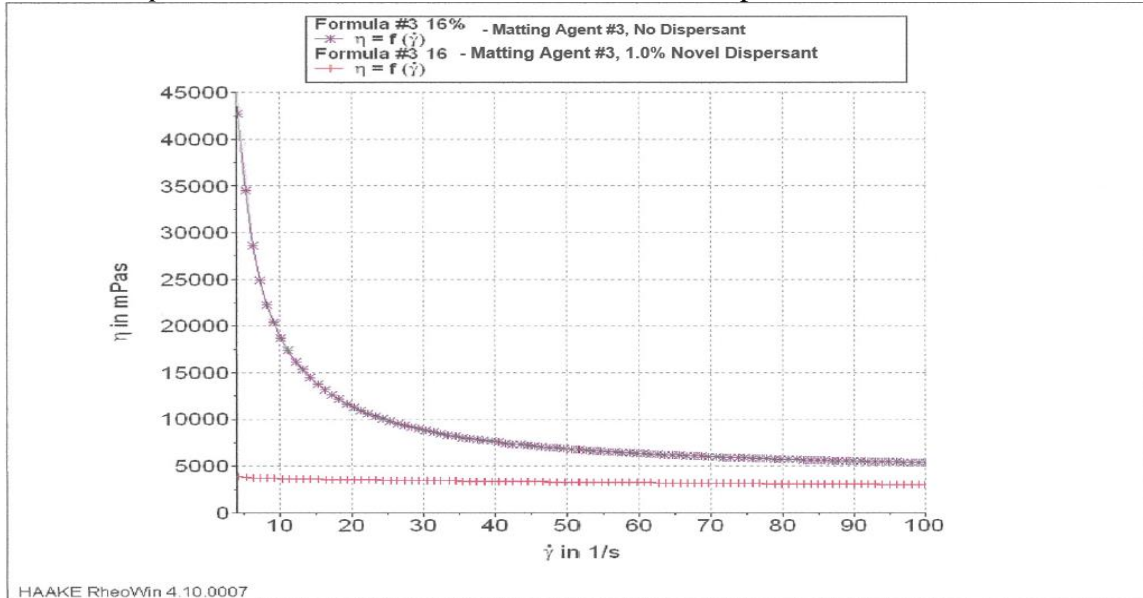
Graph #2: Formula #2 with and without novel dispersant additive



<b>Formula #2 Results</b>	<b>Blank</b>	<b>w/ additive</b>
Viscosity (4.0sec <sup>-1</sup> ), cps	27,210	3,926
Viscosity (100sec <sup>-1</sup> ), cps	3,861	3,037
Reflectometer Value (60° Angle)	-	34

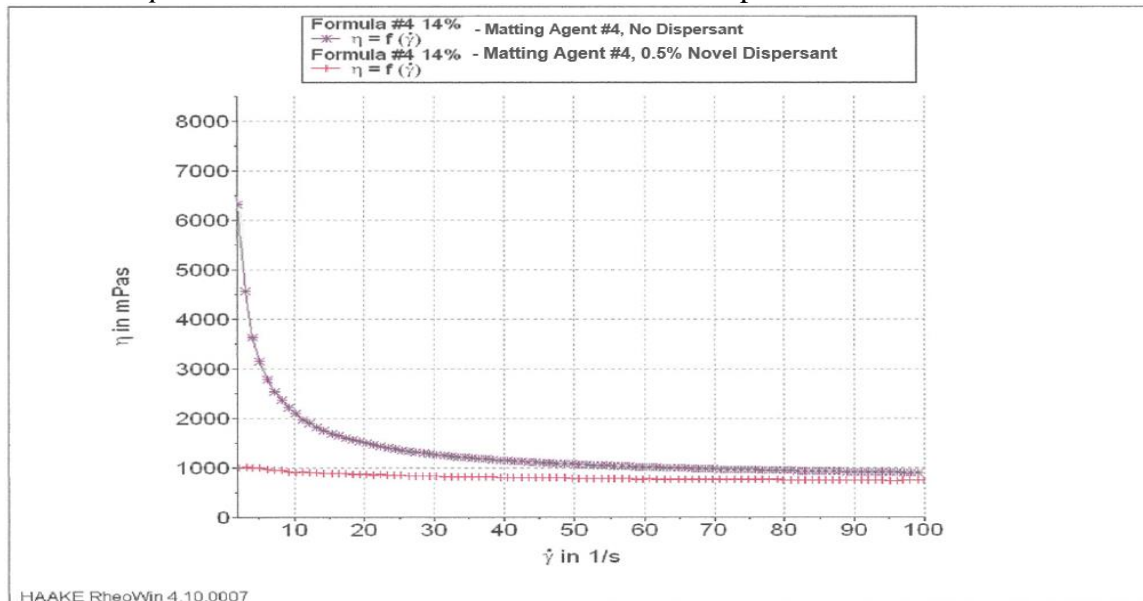


Graph #3: Formula #3 with and without novel dispersant additive



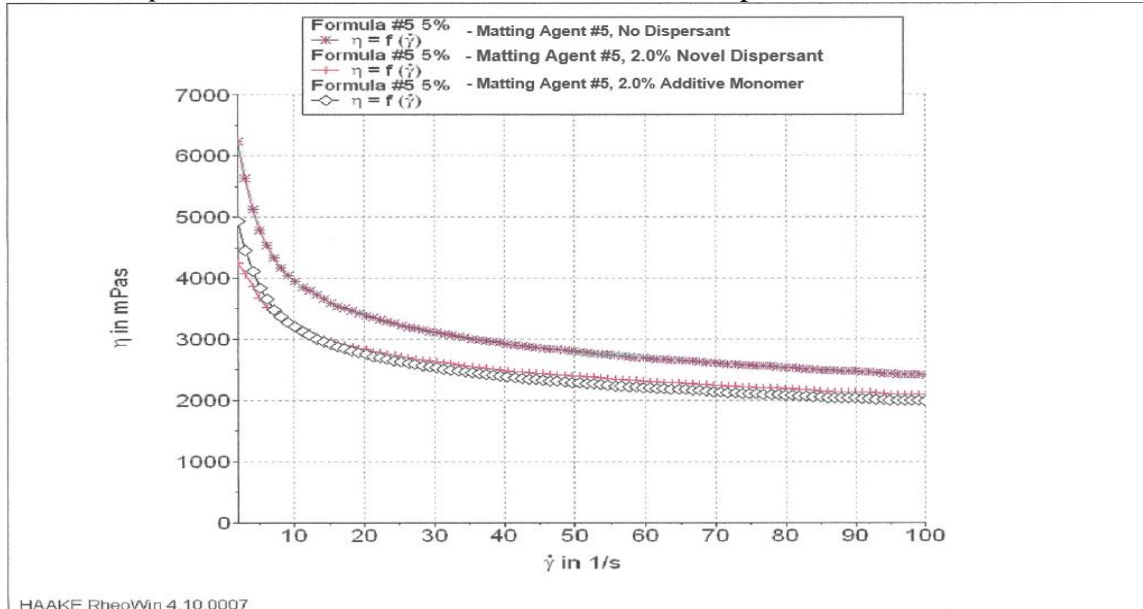
<b>Formula #3 Results</b>	<b>Blank</b>	<b>w/ additive</b>
Viscosity (4.0sec <sup>-1</sup> ), cps	42,720	3,886
Viscosity (100sec <sup>-1</sup> ), cps	5,351	3,005
Reflectometer Value (60° Angle)	-	22

Graph #4: Formula #4 with and without novel dispersant additive



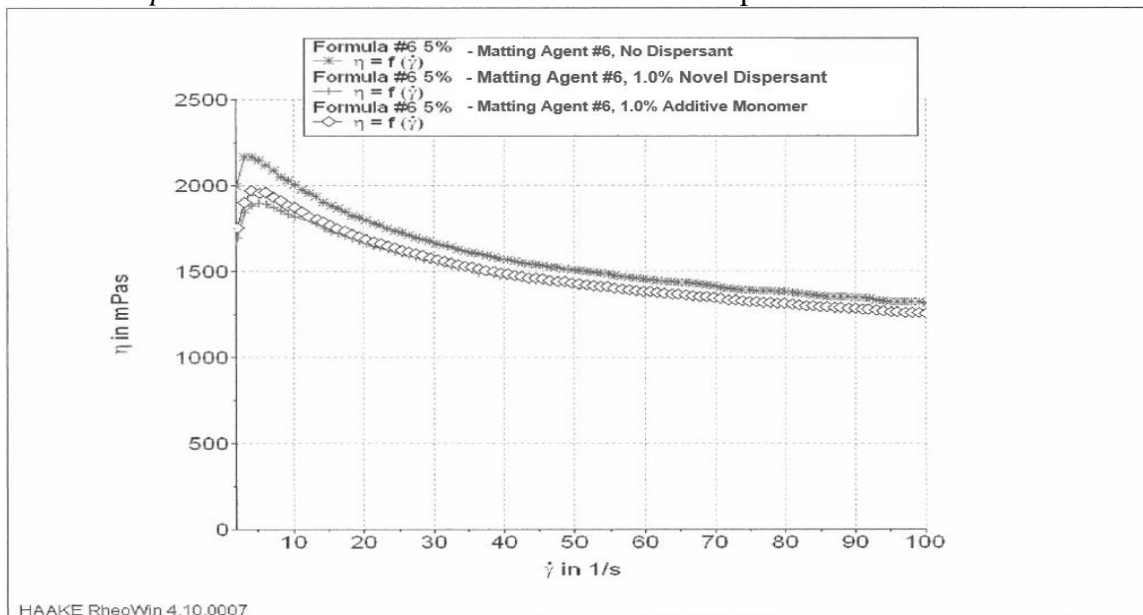
<b>Formula #4 Results</b>	<b>Blank</b>	<b>w/ additive</b>
Viscosity (2.0sec <sup>-1</sup> ), cps	6,320	999
Viscosity (100sec <sup>-1</sup> ), cps	900	739
Reflectometer Value (60° Angle)	17.5	19.0

Graph #5: Formula #5 with and without novel dispersant additive



<b>Formula #5 Results</b>	<b>Blank</b>	<b>w/ additive</b>	<b>w/ add. monomer</b>
Viscosity (2.0sec <sup>-1</sup> ), cps	6,240	4,253	4,938
Viscosity (100sec <sup>-1</sup> ), cps	2,409	2,094	1,990
Reflectometer Value (60° Angle)	31	34.5	35.0

Graph #6: Formula #6 with and without novel dispersant additive



<b>Formula #6 Results</b>	<b>Blank</b>	<b>w/ additive</b>	<b>w/ add. monomer</b>
Viscosity (2.0sec <sup>-1</sup> ), cps	1,995	1,694	1,754
Viscosity (100sec <sup>-1</sup> ), cps	1,316	1,260	1,256
Reflectometer Value (60° Angle)	29	29.0	29.0

## Results

While every formulation evaluated presented pseudoplastic or shear-thinning behavior, the addition of a novel dispersant resulted in a yield point much lower than that of the blank coating in all cases with the exception of Formulation #5 and #6 where the difference in yield point can be considered negligible.

The evaluation of Matting Agent #1 (untreated, fumed silica) resulted in a coating which is positively affected by the presence of novel dispersant technology. It is interesting to note that during the preparation of the blank coating, it was only possible to incorporate 11.3% of the necessary 14.3% of matting agent. Without the use of novel dispersant technology, it was not possible to incorporate the appropriate amount of matting agent. While this matting agent is not a good choice for matting energy-curable systems, based on incorporation difficulty and deviation from the targeted reflectometer values, it has been shown that the use of dispersing additives greatly improves its overall dispersibility.

As seen in Graph #2, the formulation containing Matting Agent #2 (wax-treated, precipitated silica) resulted in a coating which is positively affected by the presence of novel dispersant technology. The targeted viscosity range of 2000-6000cps was achieved at shear rates of  $4.0\text{sec}^{-1}$  thru  $100.0\text{sec}^{-1}$ .

Matting Agent #3 (polymer-treated, precipitated silica) performed similarly to Matting Agent #2 in the presence of a novel dispersing additive. However, by utilizing Matting Agent #3, a formulator would be able to achieve a reflectometer closer to fulfilling the criteria for a commercial matte coating.

The evaluation of Matting Agent #4 (organically-treated, silica gel) shows that this matting agent is the best choice, of the evaluated silicas, for matting energy-curable wood coating systems (Graph #4). Without the use of additives this matting agent demonstrated positive results at both low and high shear rates. However, by incorporating dispersing technology, rheological characteristics were improved by producing a matte coating which has a very narrow viscosity differential from low to high shear rates. This characteristic is indicative of an interaction between matting agent and dispersing additive which allowed near Newtonian properties to be achieved. Lastly, a viscosity of 739cps at a shear rate of  $100.0\text{sec}^{-1}$  is unprecedented in an energy-curable matte coating containing 14% matting agent, and is the best result obtained during this evaluation. Theoretically, one could add more matting agent to further decrease gloss values.

While Matting Agent #5 (aerogel, silica gel) and Matting Agent #6 (aerogel, silica gel) are functionally very similar, the evaluation of these matting agents resulted in different findings such as yield point. Although the incorporation of a novel dispersant resulted in a lower yield point in both matting agents, the novel dispersing additive had little effect (Graph #5 and #6). While viscosity fell slightly, the improvement can be considered negligible as typically radical viscosity decreases are noticed when utilizing dispersing additives. During testing of Matting Agent #5 and #6, an additional monomer loading was added to conclude that the slight decrease in viscosity was a function of adding more monomer and not the addition of novel dispersant technology.

## **Further Comments**

The investigated novel dispersant technology has been introduced to the market-place and has been successfully utilized to improve the matting capacity of energy-curable wood coatings. The novel dispersant provides a great deal of formulating latitude by enabling the formulator to improve the rheological characteristics of matte coatings containing silicon dioxide produced from nearly all commercially available methods of manufacture. While the list of available silica matting agents is nearly endless, it is likely that benefits can be realized by the incorporation of novel dispersant technology in not only wood coating systems, but also other difficult to matte energy-curable systems like graphic arts and industrial coatings. Additional testing has been completed geared towards the graphic arts industry. These studies proved that with the incorporation of a novel dispersant, viscosities below 1500cps and reflectometer values less than 10.0 can be achieved.

Although, during this study, some reflectometer values were unsuitable, novel dispersant technology can withstand greater amounts of matting agent, without compromising rheological profiles and while achieving commercially accepted gloss values. To evaluate novel dispersing additives, it is recommended to conduct a ladder-study to determine the optimum amount of dispersing additive needed to appropriately disperse the selected matting agent. In the evaluation of the formulas within this composition, effective dispersant dosing ranged substantially, but were most effective at 0.5% to 2% by total weight of the formulation.

## **Conclusion**

As demonstrated, novel dispersant technology can have a profound impact on the rheological characteristics of energy-curable, wood coatings. This technology can aid in the incorporation of matting additives that would otherwise be impossible, and can improve viscosity profiles of matte coatings which, in some cases, nearly mimic those of particle-free gloss coatings. The ability to produce matte coatings with viscosities below 2000cps and reflectometer values less than 20.0 has been a very difficult task. These benefits allow formulators greater freedom in their matting agent choices, matting agent loadings, and abilities to impart superior characteristics which were previously unattainable. As energy-curable technology continues to improve, novel dispersants like those investigated herein may aid formulators in the development of new coatings or the re-invention of coatings predominately reserved for the water- and solvent-based coatings market.

## References

1. Basics of Fumed Silica. *Technical Bulletin- Fine Particles*. (11), 1-72. (2006).
2. Evonik Matting Agents for the Coating Industry. *Technical Bulletin- Fine Particles*. (21), 1-32.
3. Evonik Industries. *Matting Agents* [Microsoft PowerPoint slides].
4. Evonik Industries. (2010). *Dispersant Technology* [Microsoft PowerPoint slides].
5. Leach, R.H. (1988). *The Printing Ink Manual*. London, England: Van Nostrand Reinhold (International) Co. Ltd.
6. Tego Chemie Service GmbH. (2007). Wetting and Dispersing Additives. *Tego Journal*, (ed. 3), 76-87
7. Wason, Satish K. (1988). Fumed Silica. *Pigment Handbook*, 1(2), 161-174.
8. Wason, Satish K. (1988). Precipitated Silica. *Pigment Handbook*, 1(2), 139-160.
9. Wason, Satish K. (1988). Silica Gels. *Pigment Handbook*, 1(2), 175-182.