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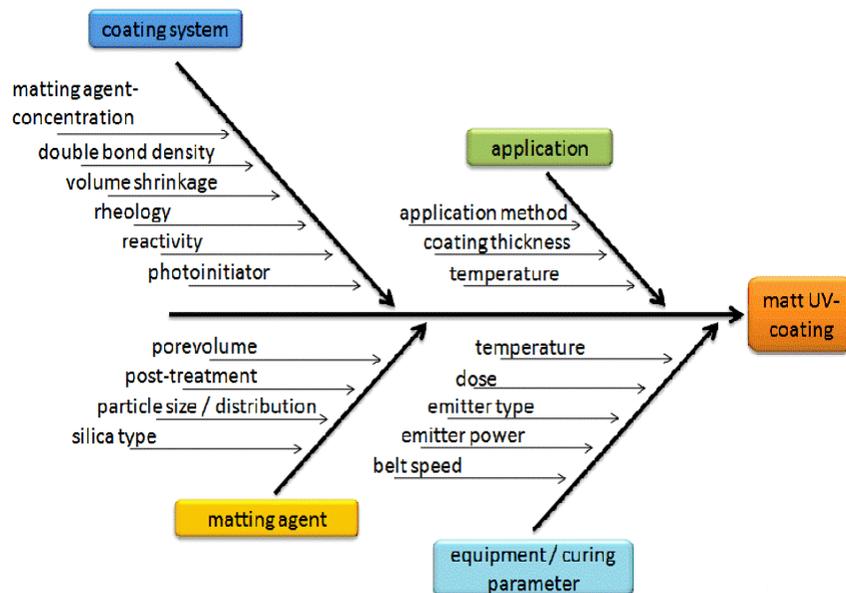
**Abstract:** While many technical advances have been made to produce low gloss, radiation curable clear coatings, they still present a challenge for most UV coatings manufacturers. Matting agents have been developed where particle size, treatment and structure have been modified to achieve low gloss. In this development, the combination of specific amorphous, synthetic silica combined with a specific Polydimethylsiloxane surface treatment was found to improve efficacy. Based on this experience, a new product especially designed for low gloss, high transparency and low viscosity was developed for UV-Coatings.

This presentation will feature results comparing this new generation of matting agent to the matting technology considered “state of the art” in UV application. The focus will be on gloss vs. viscosity behavior. Photomicroscopy based on REM and TEM-Thin-Cut will be used to demonstrate the performance of this unique new technology.

**Text:** Conventional coating systems, including waterborne and solvent based UV-curable coatings, are easily matted due to emission-related and vertical film shrinkage. However, this mechanism does not apply for solvent-free coatings, such as 100 percent UV-curable coatings, due to the absence of film shrinkage, which makes matting significantly more difficult. The coating formulator faces the task of compensating for the absence of vertical film shrinkage by suitable mechanisms for roughening the coating film surface and thus achieving desired matting. One option is to select the particle size of the matting agent used (which is generally silica), based (as far as possible) on the thickness of the applied coating film. The second option involves increasing and optimizing the volume shrinkage of the coating film, achieved by radical polymerization of the acrylate oligomers and monomers. The principle here is that the silica particles uniformly distributed in the liquid coating form a matting agent matrix / domain. During the curing process, this matting agent domain shrinks less than the surrounding binder matrix around it.

This paper will address basic aspects of what a formulator might consider to matt UV systems and Chart 1 gives an overview of details which can influence the final gloss of a UV coating. Table 1 gives the overview of formulations used.

### **CHART 1. Critical Aspects to Matting UV Coatings**



**Table 1. Formulations**

Raw material	Formulation							
	#1a	#1b	#2a	#2b	#3	#4	#5	#6
Amine-modified oligoetheracrylate #1 dm	68.51	68.51						
Amine-modified oligoetheracrylate #2 em			68.51	68.51	70.57	69.61	67.32	
Amine-modified oligoetheracrylate #3								59.46
TMPTA	17.11	17.11						
HDDA			17.11	17.11	17.62	18.25	17.65	
Monomer (Formulation #6)								25.54
Benzophenone	2.91		2.91					
$\alpha$ -Hydroxy ketone (PI #1)		1.94		1.94		2.43	2.35	3.84
Bisacyl phosphine BAPO)#2		0.97		0.97		0.49	0.47	0.45
KS #2	11.47	11.47	11.47	11.47	11.81		12.21	10.71
KS #3						9.22		
<b>Total</b>	<b>100.00</b>							

**Selected photoinitiators**

Photoinitiator	Suggested for Coatings	Chemical class	Absorption peaks ...nm
Benzophenone	X	Benzophenone	254
PI #3 (mixture of benzophenone and PI #1)	X	$\alpha$ -Hydroxy ketone	250, 332
PI #1	X	$\alpha$ -Hydroxy ketone	246, 280, 333
PI #2	X	Bisacyl phosphine (BAPO)	295, 370

**Table 2 Matting Agents Included in Study**

Matting silicas used				
	Unit	Matting agent KS1	Matting agent KS2*	Matting agent KS3
Production method		Precipitated silica		
Loss on drying	%	6	6	7
Loss on ignition	%	13	11	5
Aftertreatment		organic	PDMS	none
pH		6.0	7.0	6.0
Agglomerate particle size $d_{50}$ (laser diffraction)	$\mu\text{m}$	4.5	5.0	14.5
Tamped density	g/l	115	130	120
DBP no.	g/100g	270	275	315
Sulfate content as $\text{SO}_4$	%	1.0		0.8
$\text{SiO}_2$ content	%	98.0		98.5

Experimental details include the application was done with wire-wound rod on BYK contrast card 2854. UV-drying was done with a UV dryer M-30-2x1-MBS-URS-TR-SLC (IST Metz GmbH) with 2 separate switching and controllable lamp units. This unit is fitted with one (pure) Hg and one Fe-doped lamp. The maximum lamp power is 200W/cm, which is adjustable between 50% and

100% power. The belt speed is adjustable between 2m/min and 50m/min. The Dosimetry Lamp power is controlled with a UV dosimeter UMD 2 (IST Metz GmbH)

Overall Agenda of this paper will focus on four main areas: (1) Importance of the Coatings System, (2) Importance of the Matting Agent Technology Selection, (3) Application, (4) Equipment and Curing Parameters.

**Importance of the Coatings System:**

- Matting agent concentration

As with all other types of coatings systems, matting efficiency is not a linear function and gloss reduces as concentration goes up. The efficiency associated with a matting agent is system specific. However, there are considerations to choose a matting agent and other formulating raw material which can improve the “mattability”. System choices will be reviewed in this paper which will also highlight a new matting technology based on a precipitated silica core, having a optimized particle size, pH, morphology, and novel treatment.

- Double bond density

The double bond density is the important variable for choosing a suitable oligomer. As the DB density increases, the polymerization-related volume shrinkage also increases. Oligomers with the highest possible double bond density and a low viscosity are the most suitable. Oligomers with a low double bond density and a high viscosity could also be suitable because of their principle monomer requirements.

Matting studies have shown that the density of the double bond, which depends on the functionality and the molar mass, plays a key role. This is based on a general rule of thumb: the higher the density of the oligomer double bonds, the better the mattability of the coating. However there is an exception to every rule, and this case is no different. Oligomers with low double-bond densities and higher viscosity are also mactable, if the right monomers are used.

Calculation formula for double-bond density:

$$DB\text{-Density} = \frac{\text{Functionality [DB/Mol]}}{\text{Relative molar mass [g/Mol]}} \times 1,000 \text{ [g/kg Oligomer]} = \frac{[\text{DB}]}{[\text{kg Oligomer}]}$$

Acrylate oligomer		#2	#1
Matting capability		good	bad
Type of oligomer		Amine-modified oligoetheracrylate	Amine-modified oligoetheracrylate
Viscosity of delivery form	mPas	approx. 120	approx. 600
Reactivity (BASF method)	m/min	42	70
Molecular weight	g/mole	600	1000
Functionality	DB/mole	3,0	3,5
Double bond density	Mole DB/kg oligomer	5,0	3,5

*The double bond densities of the acrylate oligomers are in the range of 2.5 to approx. 6 mole Db/kg oligomer*

	Formulation 1a	Formulation 1b		Formulation 2a	Formulation 2b
Conditions	adverse	optimum	Conditions	adverse	optimum
60° reflectometer value	81,6	30,5	60° reflectometer value	74.3	7.2
Oligomer #1	68,51	68,51	Oligomer #2	68.51	68.51
TMPTA	17,11	17,11	HDDA	17.11	17.11
Benzophenone	2,91		Benzophenone	2.91	
PI #1		1,94	PI #1		1.94
PI #2		0,97	PI #2		0.97
KS #2	11,47	11,47	KS #2	11.47	11.47
<b>Total</b>	<b>100,00</b>	<b>100,00</b>	<b>Total</b>	<b>100.00</b>	<b>100.00</b>

- Volume shrinkage

Optimizing choices of oligomers and monomers while adjusting curing conditions to achieve highest volume shrinkage will result in matte coatings.

- Rheology

Due to the inherent difficulties associated to matte UV coatings (low - no volatile emissions and very low volume shrinkage compared to non-UV technology), typically higher levels of matting agents are used. This increased usage rate can dramatically increase formulating viscosity, which can compromise applicability. From past experience: it is known that some increase to structure viscosity has a favorable effect on matting, as well to maintain suspension and can stability, however finding this balance can be challenging.

New surface treatment technology developed can be an advantage to effective matting, and reduce viscosity build-up. Treatment based on reactive acrylated-siloxane chemistry has shown to be highly effective to reduce gloss, with only minimal influences to rheology.

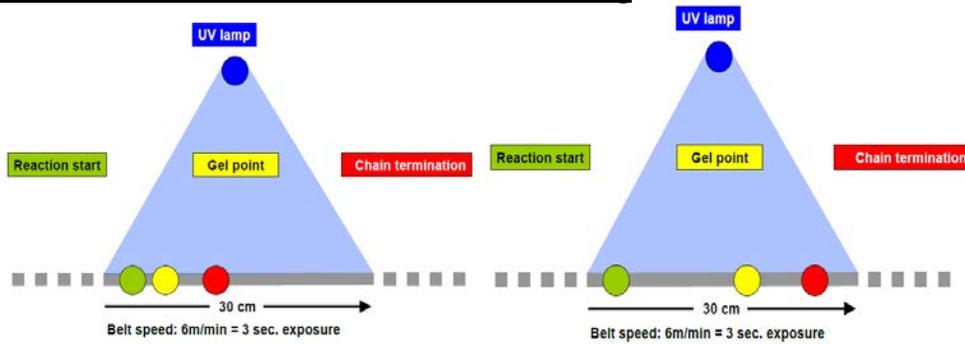
- reactivity (resins, monomers)

The key factor for “reactivity” is the timing of the polymerization process up to the gelling point. In this case, "gel point" is defined as the time when the polymerization of the binder has advanced so far that the silica and binder matrix continue shrinking in the same ratio to each other, *while the gel point generally is defined as the point where clustering to a macroscopic network begins and the viscosity is increasing significantly.* From the gel point, the agglomerates of the matting agent are fixed in the developing polymer network, and can therefore contribute nothing more to the surface roughness. The basic point here is: the later the gel point occurs, the more pronounced the matting.

The timing of the gel point depends on a number of factors; such as how fast the molar mass increases, how the segment mobility of the chain molecules or the rheological behavior changes. Consequently, other components of the formulation also have a significant influence on the mattability of UV-cured coatings; acrylate oligomers and monomers polymerize to binders, whereby the monomers in UV-cured coatings also assume the function of the solvent, as well as the photoinitiators have influence.

The matting effect can be improved considerably by choosing suitable monomers. When choosing monomers, their behavior in regards to influencing chemical and mechanical properties as well as reactivity must be considered. In spite of having high double bond densities, trifunctional monomers appear to be less suitable – probably because of the lower conversion. Chart 2 highlights a simple model for improving mattability.

## Chart 2 Gel Point Model for Bad and Good Matting

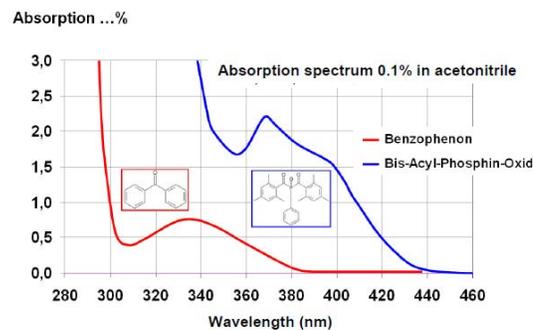


- Photoinitiator choice

The photoinitiator is another parameter influencing mattability during formulation of the coating. “Surface driers” (such as benzophenone) with absorption maxima mainly at the short-wave region (that dry the coating film very quickly from the surface down), promote gloss, while driers with absorptions in the long-wave range (figure 1) promote a significantly more even and prolonged hardening of the coating layer. The gel point, therefore, occurs at a later time - which is desirable.

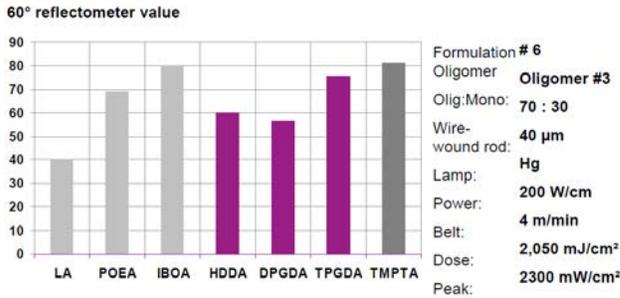
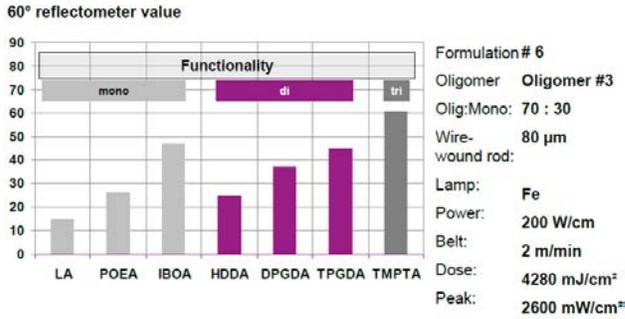
Choosing the right photoinitiator, in the right (lowest possible) concentration is very important. Most suitable are mixtures of photoinitiators with mainly short/medium-wave absorption spectrums and photoinitiators with long-wave absorption spectrums (due to low gradient formation during polymerization). Photoinitiators with strong surface drying (e.g., BP) support high gloss and are detrimental to matting.

**Figure 1. Schematic of the absorption curves of various photoinitiators**



Experiments with different monomers have shown that their contribution to matting depends on the shape of the molecule and the conversion rate during polymerization. Monomer molecules with a predominantly linear, chain-like shape promote matting and are recommended because they have higher mobility and better conversion rates. Conversely, three-dimensionally shaped or branched monomers have reduced mobility because of steric hindrance, as well as lower conversion rates, which make them more difficult for matting. In this model, a highly branched monomer shrinks with the silica matrix, thereby compromising it and achieving low gloss ranges (high surface roughness) is much more difficult.

**Figures 2 and 3 depict Monomer, Lamp, Dose, Peak Effects on Gloss**



**Importance of the Matting Agent Technology Selection**

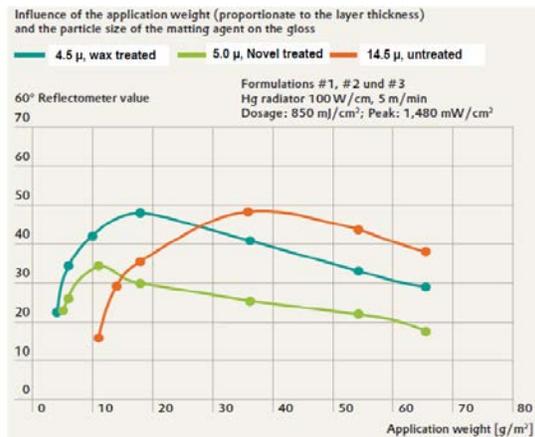
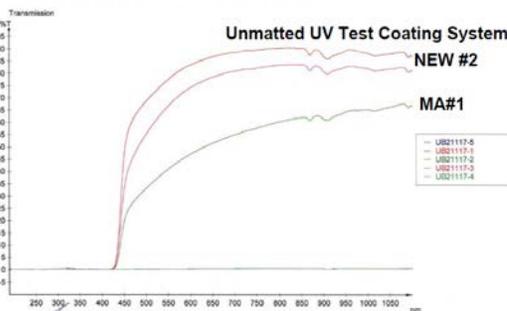
- Pore volume

Pore volume, while influencing absorption capacity, can increase viscosity. However, it is a parameter which can also aide in achieving low gloss, as it serves to create strong domains around matting agents, as binder is absorbed. Higher pore volume can also support suspension providing improved can stability.

- Post treatment

Various surface treatments can be applied to matting agents to improve suspension behavior, reduce hard settling, reduce thickening effects and to improve compatibility with a particular coating's chemistry. The new treated grade in the following schematics highlight the new technology treated with a novel siloxane optimized for UV coatings. This new technology has a far more efficient performance over a wide application weight and improved clarity and compatibility in UV systems.

**UV-VIS Transmission of Novel grade #4 to Matting Technologies on the market**



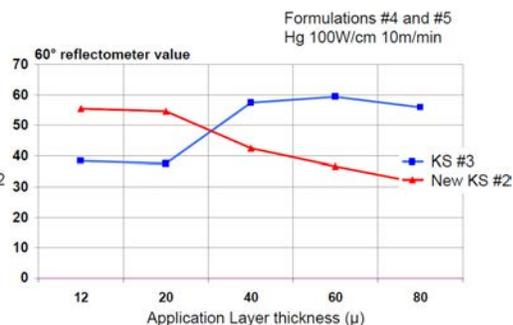
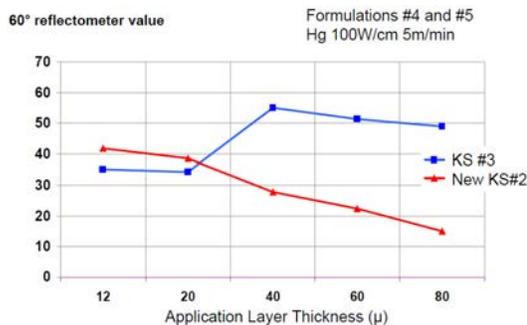
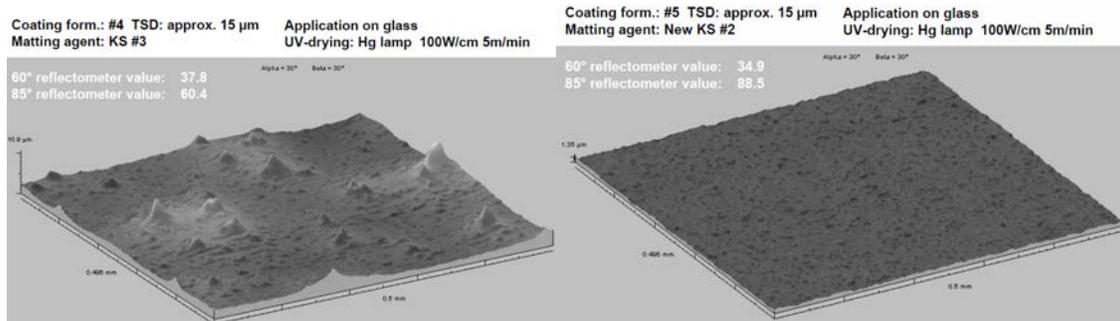
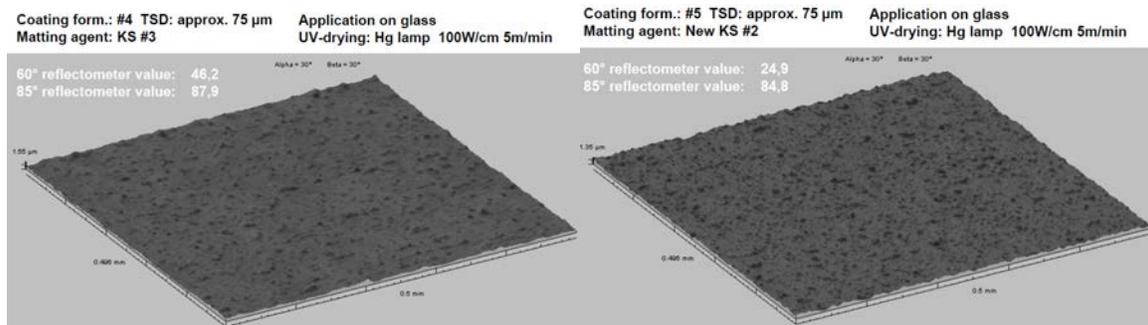
- Particle size and distribution

Matting thin layers: With application of thin layers of coating (max. 20µm) the particle size of the matting agent has to be adjusted to the thickness of the coating layer. Recommended particle size:  $d_{50} = 0.5$  to 1 times the thickness of the dry layer.

Matting thick layers: With application of thick layers of coating ( $\geq 20 \mu\text{m}$ ), it is advisable to use fine matting agents. Recommended particle size:  $d_{50} \leq 6 \mu\text{m}$

The following model depicts the New Matting Technology #2 due to its Novel treatment combined with side and structure gives similar performance to much larger size technology, with the added benefits of improved clarity and lower viscosity resulting from the novel treatment.

Resulting surface topography relates to particle size and distribution. Profiles demonstrate performance at different film thicknesses.



## Application

- Thickness

UV systems behaved different than other types of coatings in that thicker films are easier to matte than thin films and in any case typically require higher loading of matting agents. Particle size and treatment of matting agent can be optimized with formulating adjustments to achieve matting over a wide range of film thickness. Sections on matting agents and Coating System details further discuss specifics to be considered.

- Temperature

From past experience: "pre-heating" the substrate and the applied coating film has a favorable effect on matting.

### Equipment and Curing Parameters

The actual curing process also provides additional opportunities for reducing the gloss of a coating film. Here, parameters such as: the type and emissions spectrum of the light source, intensity and irradiation times, geometry of the radiation source, ambient temperature and type of substrate play a role. These influential factors were investigated and the following details can be considered to achieve matte UV finishes.

- Temperature

From past experience: "pre-heating" the substrate and the applied coating film has a favorable effect on matting

- Dose

Dose = Intensity \* t      mJ/cm<sup>2</sup> : Radiation that has an effect on a sample when it passes through. The dose is inversely proportional to the belt speed

Intensity = Power/Distance<sup>2</sup>      mW/cm<sup>2</sup> : Effective radiation per surface area. The peak is independent from the belt speed. The peak could be described as the lamp's "fingerprint"

**Note about dosimetry:** Dose and peak needs to be specified Dosimeters from different manufacturers cannot be compared directly in terms of their measuring results

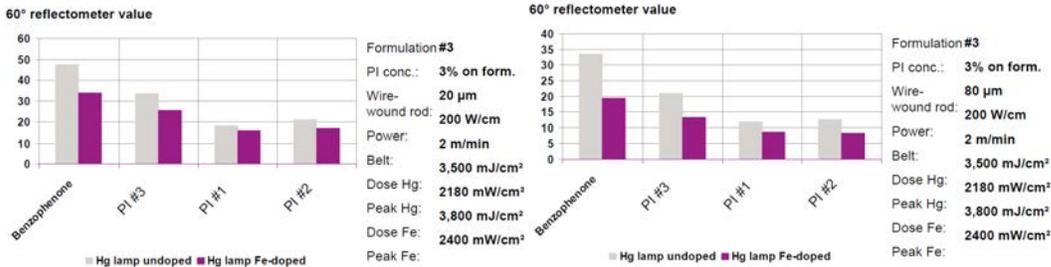
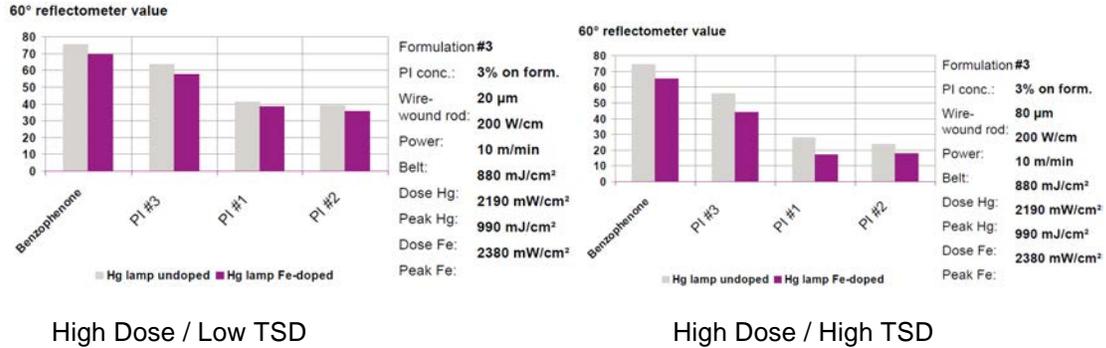
- Emitter type and power

Influence of the light spectrum using a Fe-doped lamp produces a significantly better matting effect than a pure Hg lamp. Due to the visible shift in the spectral distribution of the radiation towards the longer wave range, a more even penetration of the coating with less gradient formation during polymerization is achieved. Formulators should remember: Fe doping creates a slightly lower reactivity and may require an adjustment in photoinitiation

### Influence of Radiation Spectrum on Gloss

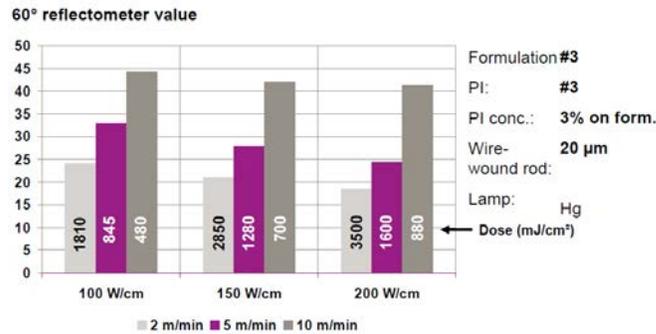
Average dose / Low TSD

Average dose / High TSD



- Belt speed

With the same dose, the belt speed rather than peak energy is the important variable in terms of matting. This address the assumption that matting is improved by delaying the gel point (in the millisecond range). Chart below depicts the influence of dose via belt speed on gloss.



### General Recommendation for low gloss of UV cured coatings:

With the increasing popularity and wide spread use of UV-cured coatings, formulators are searching for effective and efficient ways to reduce gloss. The advantages are well known that these type coatings require little energy but also little time to cure and the coated object is ready for downstream processing just a few seconds after curing. The fast processing time which can coat many object and parts in an efficient manner brings a powerful cost benefit driver to the increasing popularity.

To achieve matte UV-cured coating, formulators are suggested to:

- choose an oligomer with a high DB density
- choose a suitable monomer, photoinitiators with balanced surface and inside drying mechanisms.
- Formulate the "complete package" oligomer/ monomer/ initiator, so that the reactivity of the coating is just above the required reactivity (approx. +20%).

- Choose a matting agent to suit the layer thickness.
- Choose the highest possible drying energy at lowest possible belt speed (remember: cost effectiveness)
- Cure in one pass.

To facilitate matting, a new reactive siloxane treated, precipitated silica technology represented by KS #2 gives the UV coatings formulator a new and novel option to achieve low gloss finishes, while maintaining low applications viscosity, high clarity & transparency and achieving high surface smoothness.

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