INFLUENCE OF SYNTHETIC SILICA ON THE MATTING OF 100% UV – COATINGS

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1. Introduction

Radiation-curable coating systems are gaining ground in an increasing number of applications, thanks to their favorable emission behavior. The most important market segment in Europe is the wood coating sector with over 14%.

Matted coatings, varying from very dull to satin gloss, dominate in the wood and furniture coating sector. The matting of 100% UV coatings still presents a major challenge to every paint technician, whereas the matting of solvent-containing or aqueous coatings poses no problem [1].
The problems are due to the virtual absence of film shrinkage in the 100% UV coatings during the curing of the system.

2. Theoretical Analysis

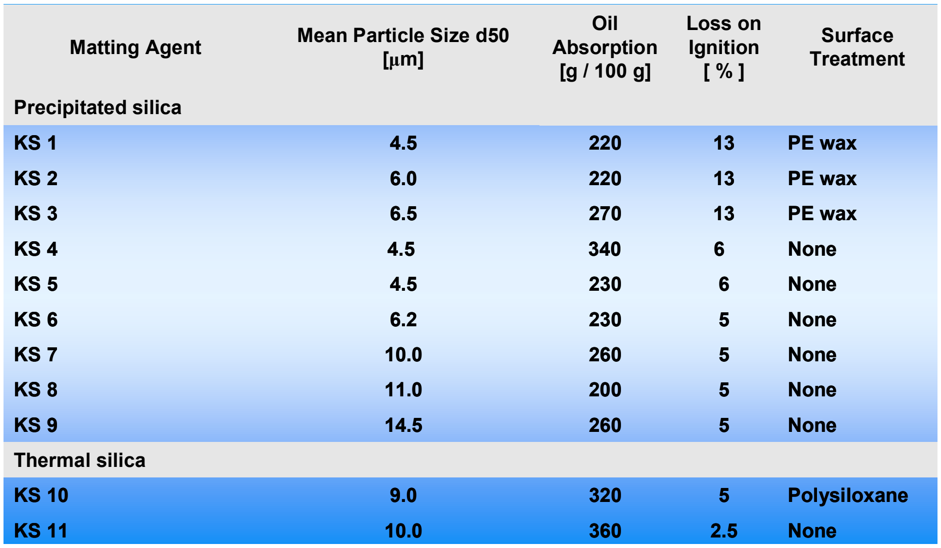
The goal of this study, which was conducted in conjunction with a graduate thesis, was to determine the causes and possible variables of the matting of UV coatings.
To keep the parameters as small as possible, three oligoether acrylates with different reactivities were selected. Tested for this purpose were oligomers (BASF AG), and three different monomers. A combination of 1-hydroxy-cyclohexyl-phenyl-ketone and Bis [2,4,6-trimethylbenzoyl] phenylphosphineoxide were used as an initiator.

		Reactivity [m/min]	Double Bond Content [mol DB / kg of resin]	Viscosity [mPas]
	Oligomer Typ			
1	**Oligoether Acrylate**	**3**	**6.54**	**83**
2	**Amine-modified Oligoether acrylate**	**12**	**6.14**	**99**
3	**Amine-modified Oligoether acrylate**	**14**	**5.74**	**105**
	Monomer			
HDDA	**Hexanediol Diacrylate**	**-**	**8.7**	**6**
TPGDA	**Tripropylene Glycol Diacrylate**	**-**	**6.7**	**11**
IBOA	**Isobornyl Acrylate**	**-**	**5.0**	**130**

* all datas are related to an blend of oligomer / HDDA = 80:20

Table 1 Choice of oligomers and monomers

Classified silicas manufactured by precipitation or thermal processes were selected as the matting agent [2] as shown in Table 2.



Matting Agent	Mean Particle Size d50 [µm]	Oil Absorption [g / 100 g]	Loss on Ignition [%]	Surface Treatment
Precipitated silica				
KS 1	4.5	220	13	PE wax
KS 2	6.0	220	13	PE wax
KS 3	6.5	270	13	PE wax
KS 4	4.5	340	6	None
KS 5	4.5	230	6	None
KS 6	6.2	230	5	None
KS 7	10.0	260	5	None
KS 8	11.0	200	5	None
KS 9	14.5	260	5	None
Thermal silica				
KS 10	9.0	320	5	Polysiloxane
KS 11	10.0	360	2.5	None

Table 2 Choice of different matting agents

The following data generally applied to the matting of 100% UV coatings [3, 4, 5]:

- Low-viscosity and low-reactive oligomers can be matted relatively easily.
- Coating films with higher film thickness are harder to matt.
- Matting agents with a strong thickening action have less matting efficiency.
- Preheating the matted coating film to be cured improves the degree of matting.
- Low belt speeds with low radiation source output improve the degree of matting.

The following parameters were investigated in this study:

1. Influence of monomers on gloss.
2. Influence of particle size and surface treatment of the matting agent.
3. Influence of oligomer reactivity and double bond content.
4. Influence of bimodal particle size distribution

A total of three test formulations, which are shown in table 3, were used in this study.
At this point, we need to stress that these formulations are purely models and are not of practical interest.

Raw Material	Parts by weight		
	Form. 1	Form 2	Form 3
Oligomer 1	71.3		
Oligomer 2		74.4	
Oligomer 3			93.0
Monomer 1 (HDDA)			
Monomer 2 (TPGDA)			
Monomer 3 (IBOA)			
Matting Agent	8.2	4.2	4.2
Irgacure 184	2.3	2.4	2.4
Irgacure 819	0.4	0.4	0.4
Total	100.0	100.0	100.0

Table 3: General Test Formulations

3. Experimental Part

3.1 Influence of Monomers and Oligomers on the Gloss of Matted UV Coatings

Formulation 1 was used as the test formulation, with oligomer and monomer 1 (HDDA) combined in the ration of 80:20. Curing was conducted using a UV system by the company IST Metz GmbH (Nürtingen) at a belt speed of 3 m/min and a radiation source power of 100 W/cm. For evaluation, silica 1 was compared with silica 3 in oligomers 01 and 03 at 80 µm and 15 µm for matting efficiency.

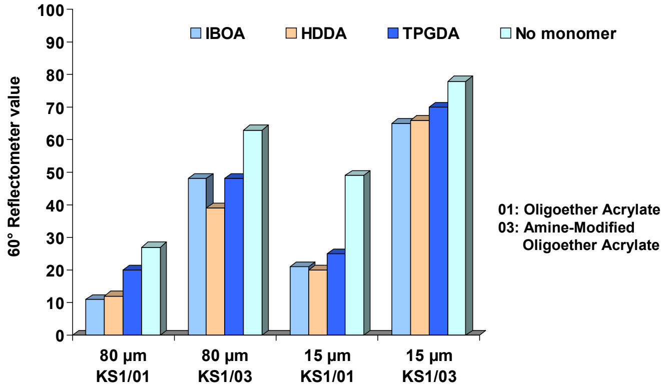


Figure 1 Gloss levels based on formulation UV 1, matting agent: 8.2% KS 1: oligomer 01, 03

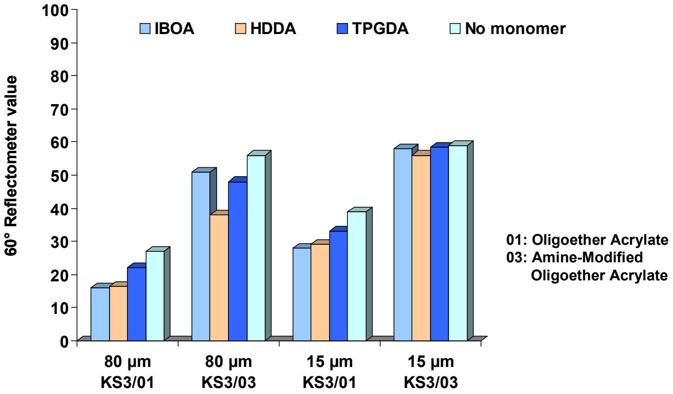


Figure 2 **Gloss levels based on formulation UV 1, matting agent: 8.2% KS 3: oligomer 01, 03**

Coatings without reactive thinners, or monomers matted with a fine particle size matting agent (silica 1) have considerably higher gloss levels particularly when higher reactive oligomers are used as shown in Figure 1, whereas a coarser silica (silica 3) performs somewhat better in matting efficiency, particularly at small film thicknesses and high reactive oligomers (Figure 2). Non-surface-treated silicas such as silica 5 and silica 6 show practically the same behavior but behave somewhat worse than surface-treated matting agents because of their thickening action.

3.2 Influence of Particle Size and Surface Coverage of the Matting Agent

In this test series, precipitated surface-treated silicas with particle sizes in d_{50} of 4.5 µm and 6 µm were compared with precipitated untreated silicas. The selected silicas were based on the same silica. The UV 2 formulation was selected in a combination with monomer 3 (IBOA).
Generally the matting efficiency of an untreated silica is greater than that of its post-treated counterpart. At higher film thicknesses, the post-treated types showed distinct advantages in terms of gloss and viscosity. If the particle size of the silicas with relation to matting efficiency is compared the finely devided matting agent has higher efficiency at high film thicknesses than the matting agent with coarser particles, and this regardless of surface treatment. These datas are shown in Figure 3 a and 3 b.

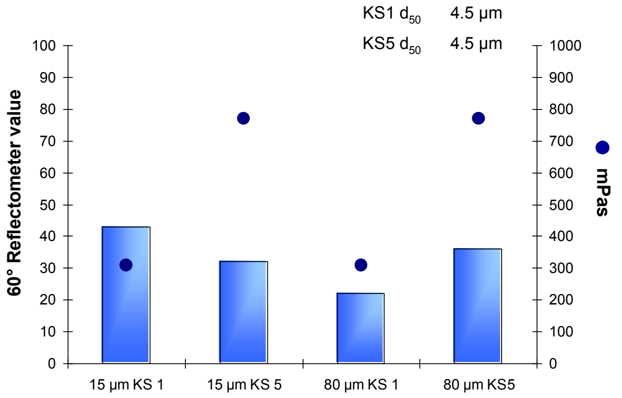


Figure 3a **Influence of surface treatment of silicas on gloss and rheology (concentration used 9.5%)**

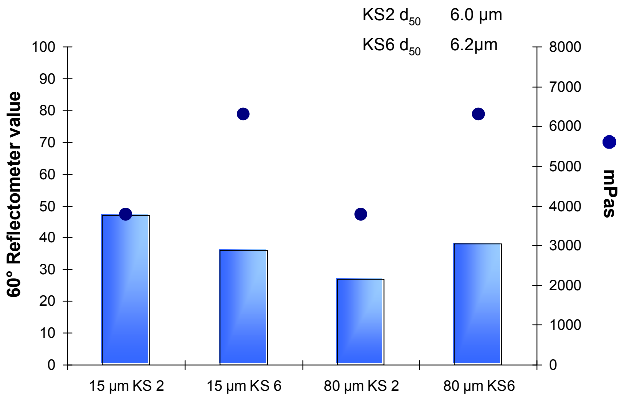


Figure 3b **Influence of surface treatment of silicas on gloss and rheology (concentration used 9.5%)**

In another test, as shown in Figure 3 c, an untreated thermal silica was compared with a thermal silica post-treated with polysiloxane.

The mean particle size d_{50} hardly varies, although the oil absorption value of the polysiloxane-treated matting agent is considerably reduced, which should at least influence the rheology. Although thermal silicas permit using only low concentrations of approx. 5–7% Matting Agent because of their looser agglomerate structure and their greater particle size distribution in comparison to precipitated silicas but still at this low percentage of Matting Agent, they feature excellent matting efficiency.

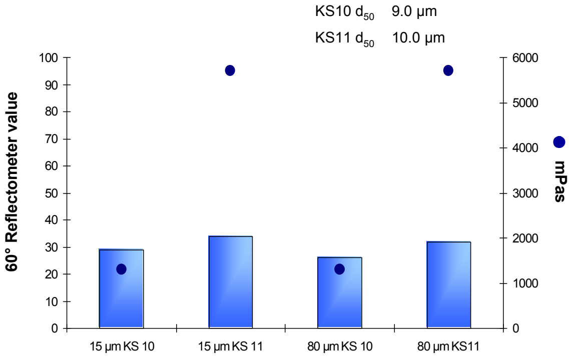


Figure 3c **Comparison of gloss and rheology at the same applied concentration of thermal silicas**

Particularly the polysiloxane-modified variant exhibits an attractive spectrum of properties, which is, unfortunately, beyond the scope of this paper.

3.3 Influence of Oligomer Double Bond Content and Reactivity

Finally, in numerous screening tests, silicas 1 and 10 were selected as models for further experiments. Regardless of silica types, matting efficiency was found to decrease – independently of film thickness – with the exception of the reactivity of the system. The thermal silica (KS 10) post-treated with polysiloxane performs at low applied concentrations comparably with precipitated silicas, although the transparency of the clear coating is significantly higher.
To test the influence of the double bond content in the system, oligomer 3 (highly active) was mixed with a low-activity oligomer and a trial was conducted with the double bond content adjusted from approx. 5.7 to approx. 6.7 mol DB/kg of resin as demonstrated in Figure 4.

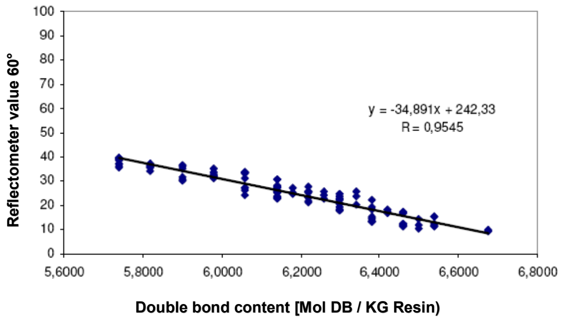


Figure 4 **Gloss level as a function of double bond content at 80 µm Wet film thickness. KS 1 was used as the matting agent.**

The gloss generally decreases with increasing double bond content, but viscosity also plays an important part in this. This means that, at the same reactivity, lower-viscosity settings cause a lower gloss level.

3.4 Influence of bimodal particle size distribution

Blends of a fine particle size silica (KS 1) with a coarse particle size silica (KS 9) where tested in formulation 1.
Several different blends of a.m. silicas where screened and for this paper the blends of 90:10; 50:50 and 10:90 are chosen and discussed.

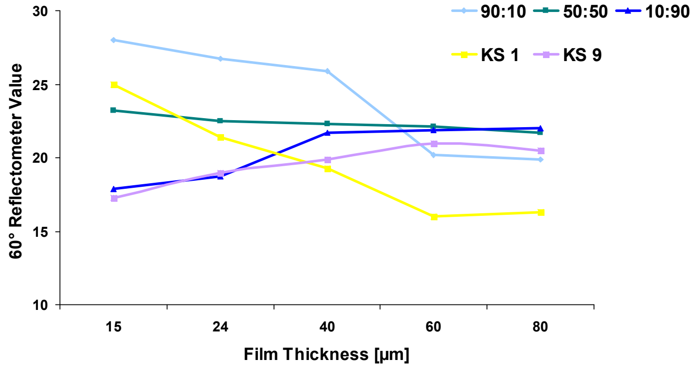
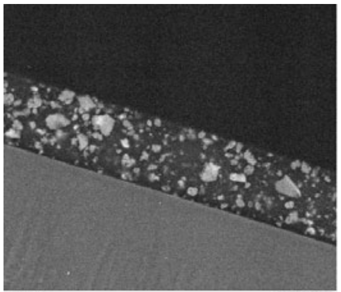


Figure 5 **Influence of the Matting Agent blends vs. KS 1 and KS 9 on matting efficiency**

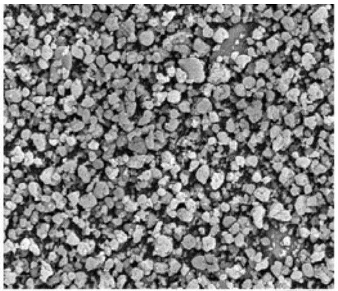
As shown in Figure 5 the blend 50:50 of fine particle size silica and coarse particle size silica shows the lowest impact of gloss at different film thicknesses. This effect could be also confirmed in formulation 2.

In picture 1 the dispersed bimodal particles could be seen in UV-lacquer by using a thin vertical film cut at a magnificent of 1000:1. By using plasma etching of the cured polymer it is possible to eliminate the coatings surface and to expose the first layers of silica particles (Picture 2 – 4). This allows us to see how homogenous the particles do roughen the coatings surface.

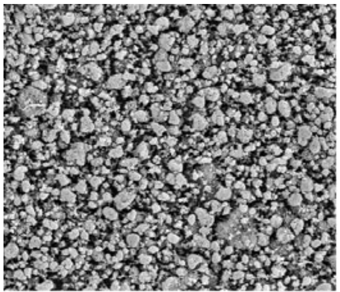
Picture 2 really represents more or less only fine particles of approx. 4 – 6 µm. Picture 4 contrary presents a high amount of coarse particles of approx. 10 – 20 m. On the other hand picture 3 shows a well balanced distribution of fine and coarse particles which at the end explains the interesting performance discussed before.



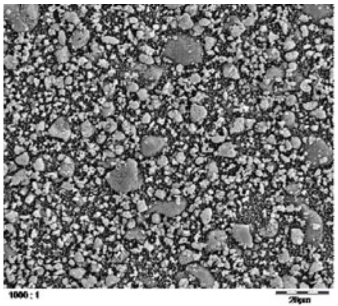
Pic. 1 Film 50:50



Pic. 2 Film 90:10



Pic. 3 Film 50:50



Pic. 4 Film 10:90

Summary

The matting of 100% UV coatings is still a complex issue for the coating chemist. This study also fails to provide a specific conclusion as to what type of matting agent is the product of choice. However, the study does indeed show how complex the coating chemist's problem is. Nonetheless, several key points can be inferred from this study

In particular the polysiloxane modified variant exhibits an attractive spectrum of properties. Finally, in numerous screening tests, a precipitated silica and the thermal polysiloxane treated silica (KS10) were selected as models for further experiments. Regardless of silica types, matting efficiency was found to decrease – independently of the film thickness – with the exception of the reactivity of the system. The polysiloxane modified silica has a performance at low concentrations comparable with precipitated silica's similar or even smaller particle size e.g.(KS 10): Gloss 30 @

60°and a viscosity of 2000mPas and precipitated silica (KS 2): Gloss 45@ 60° and a viscosity of 4000mPas.

Although the transparency of the clear coating with KS 10 is significantly higher. The transparency or density was measured according DIN 16536-1. At the same dry film thickness of 60 µm the density of the clear coat matted with KS 10 was 1,81 and for the matted clear coat with KS 2 a density was measured of 1,68. Already a difference of the density of 0,1 is considered as significant different!

Bimodal particle sizes of silicas can even further improve the matting of coating in terms of a balanced gloss value at different film thicknesses.

Also the influence of the specific thermal conductivity and capacity of the substrate was studied. Different substrates like paperboard, glass, PMMA and wood was tested. A lower specific thermal conductivity like wood or PMMA has a positive influence on matting. In general paper board delivers the highest variation in gloss readings. In principle deep black PMMA sheets and wood are preferred as testing substrates.

- Finely classified silicas show good matting efficiency;
- Novel polysiloxane-modified thermal silicas have an attractive property spectrum of matting efficiency, transparency and rheology;
- The reactivity, double bond content and viscosity of the oligomer can have a significant influence on the matting efficiency of the silica;
- The substrate and its specific thermal capacity and specific thermal conductivity have a critical effect on the degree of matting of the coated object. A low specific thermal conductivity favors matting.
- Matting can vary depending on the medium (oligomer or monomer) in which the matting agent has been dispersed.
- Bimodal particle sizes of silicas will influence positively the gloss level at different film thickness
- Viscosity and especially the intrinsic viscosity play a significant role

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