Novel Matting Agent for Low Gloss UV Coatings

Hans-Dieter Christian, Reinhard Behl, Andreas Feller, Maria Nargiello, Evonik Degussa GmbH, Germany

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

Matting agents or additives to increase surface roughness have evolved over the decades based on a variety of sources, including ground polymeric types to those based on silicon dioxide. This paper and presentation will focus on those based on SiO_2 from precipitated and gel processes, which are marketed specifically for the UV coatings segment. This coatings segment presents its own unique challenges to achieve low gloss finishes compared to other coatings segments because there is typically no solvent, little film shrinkage, varying line speeds and curing conditions. The new matting technology noted as Matted Agent #4 will be compared to those currently available on the market.

A summary of the agenda is as follows and noted on slide 2.

Physical-chemical review of grades included
- New vs market standards

Performance properties compared
- Efficiency
- Gloss @ 60°/ 85°
- Viscosity
- Transparency
- Surface roughness

The presentation first outlines typical physical-chemical properties of the matting agents included in the study and then reviews the formulation used and data pertaining to performance. Values tested include: matting efficiency @ 60° and 85°, viscosit y build-up which is a major consideration in UV coatings especially when trying to achieve low gloss finishes in the area of 10 @ 60°. Other results presented pertain to: transparency, surface smoothness and morphological differences in technology as assessed through SEM analysis of films.

Slide 3 compares the physico chemical data of products tested.

	MA#1	MA#2	MA#3	NEW#4	MA#5	MA#6	MA#7	MA#8
Target	UV	GP	UV	UV	UV	UV	UV	UV
base	SiO2	SiO2	SiO2	SiO2	SiO2	SiO2	SiO2	SiO2
type	fumed	precip	Si Gel	precip	Si Gel	Si Gel	Si Gel	Si Gel
APS*	9	4.5	11	5	5.5	7.5	4.8 - 5.8	4.8 - 5.8
pH	7.9	6	3.5	7	7	3.5	6 - 8	6 - 8
Surface treatment	reactive siloxane #1	wax	wax	NEW reactive siloxane #2	wax	wax	organic treated	organic treated

*average particle size @ per manufacturer

Matting agents of this class vary in particle sizes, pH, morphology, and treatment types. The main innovation differentiating matting agent #4 to other current technology available is the new reactive siloxane treatment with acrylate functionality which adds greater compatibility in UV coatings systems.

Matting agents were all added at varying levels to achieve gloss of 15@60°. Once the gloss level was fixed; matting efficiency, viscosity build-up and transparency were all assessed.

Formulation used for study:

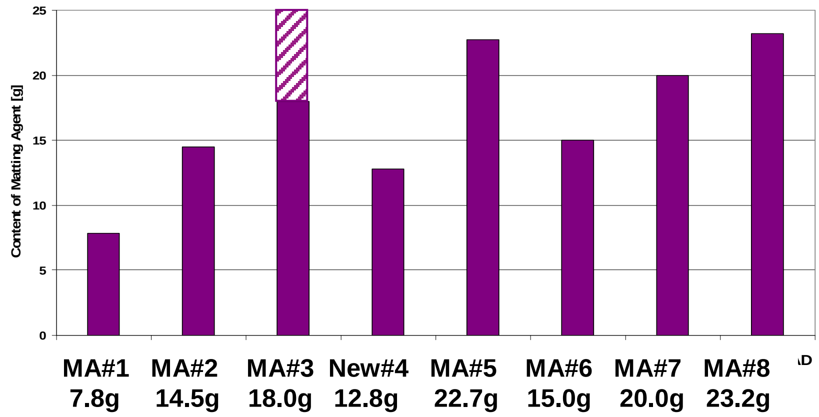
UV Test Coating System	Content (%]
Laromer® LR 8889 (Aminomodified Polyether Acrylate)	77,70
Laromer® HDDA (Hexandiol diacrylate)	19,40
Irgacure 184 (Photoinitiator)	2,50
Irgacure 819 (Photoinitiator)	0,40
Total	100,00

Formulation used for wood panels on title page of presentation:

UV Formulation used for Roller Coatings Wood Panels	
Laromer PO 43F	80,5
DPGDA	14,2
Byk 055	1,5
Darocure 1173	3,8
Total [%]	**100,00**

To achieve this gloss range, loadings varied for the eight grades tested from a low level of 7.8g to 23.2g. Matting agent #3 showed a very high viscosity increase when transitioning down from a gloss level of 25 to the target area of 15 @ 60°. The hi gher formulation viscosity encountered presented several application problems which will be highlighted in the SEM analysis later in this presentation. Slide 4 highlights the comparison of loading differences to achieve the target gloss range.

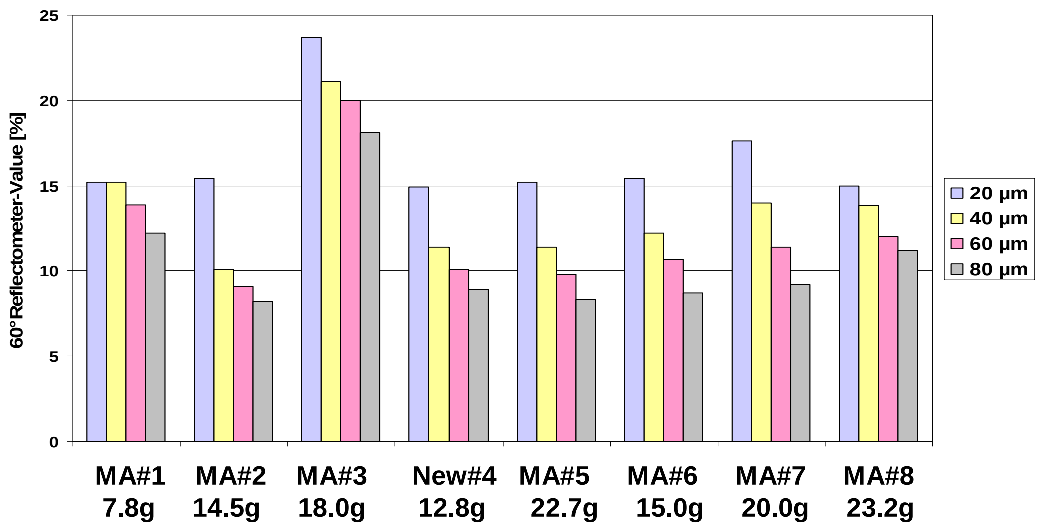
Comparison of Loading to Achieve: ***gloss of 15@60°, 15µm dft***



Clarity in the formulation itself is loading level dependent however is also a function of the treatment type. Slides 6 and 7 show a visual comparison of grades tested. The point to note is the very high clarity of this system matted with the new technology designated MA#4 in this study. This high clarity is directly due to its *novel* acrylate functional siloxane treatment and lower loading level needed to achieve the gloss target. UV-Vis transmission curve comparison on slide 8 also demonstrates that even though there is 12.8g needed to achieve this gloss range, there is little reduction in the transmission curve and the shape mirrors the UV coating system almost identically with no matting agent.

Slides 9 and 10 present the gloss data at 60° and 85° over 4 different film thicknesses of 20, 40, 60 and 80 microns. Coatings were applied by wire wound rod to BYK contrast cards no. 2854. Matting efficiency in UV systems is dependent on several factors, and certainly the physical-chemical properties of the matting agents themselves are influential. Average particle size and surface treatment play a major role. The choice of initiators, level of reactivity of oligomers and line speed of curing are also critical factors to consider when matting UV coatings.

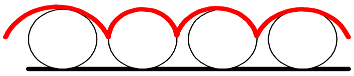
Matting Efficiency Comparison of 60° at Different Film Thicknesses



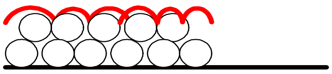
Concerning sequence of addition, matting agents were added and dispersed after photoinitiators are added. They also can be premixed with monomers. Typically, dispersants are not suggested, as they could act to reduce matting efficiency.

Typically, fast line speed and highly reactive oligomers lead to higher gloss. Slower line speed, allowing for better orientation, combined with the use of lower reactive oligomers will contribute to improved matting. In this system and in the system used to create the panels on the front slide of this presentation we worked with two different initiators, taking advantage of the different sensitivities to the wavelengths. Irgacure 184 is used for shorter wavelengths, while Irgacure 819 (normally used for pigmented coatings) is specialized for longer wavelengths. In matted clear coatings the Irgacure 819 has an advantageous influence on the curing process for thicker films. This leads to a higher film shrinkage and results in improved matting efficiency (lower gloss). Generally it is recommended to use these initiator combinations for thicker films.

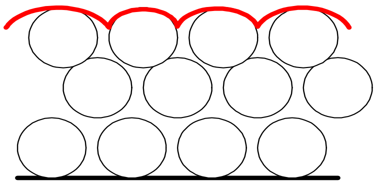
An interesting trend for matting UV coatings, which differs from matting other types of coatings, is we observe gloss decreases as film thickness increases. In UV systems, the higher the film thickness, the higher the related film shrinkage effect. To achieve low gloss, the goal is to have the highest volume-shrinkage combined with the highest packing density of matting agent. Film shrinkage comparatively speaking for UV systems is somewhat limited compared to other technologies, and we observe finer matting agents are more effective to reduce 60° gloss in thicker films.



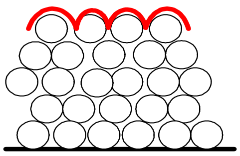
coarse matting agent – low layer thickness



fine matting agent – low layer thickness

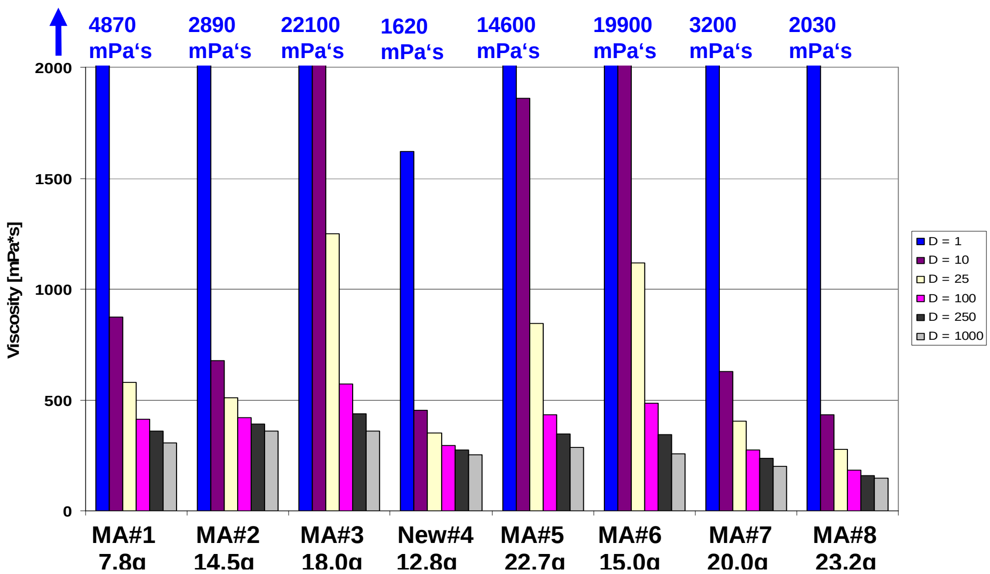


coarse matting agent – high layer thickness



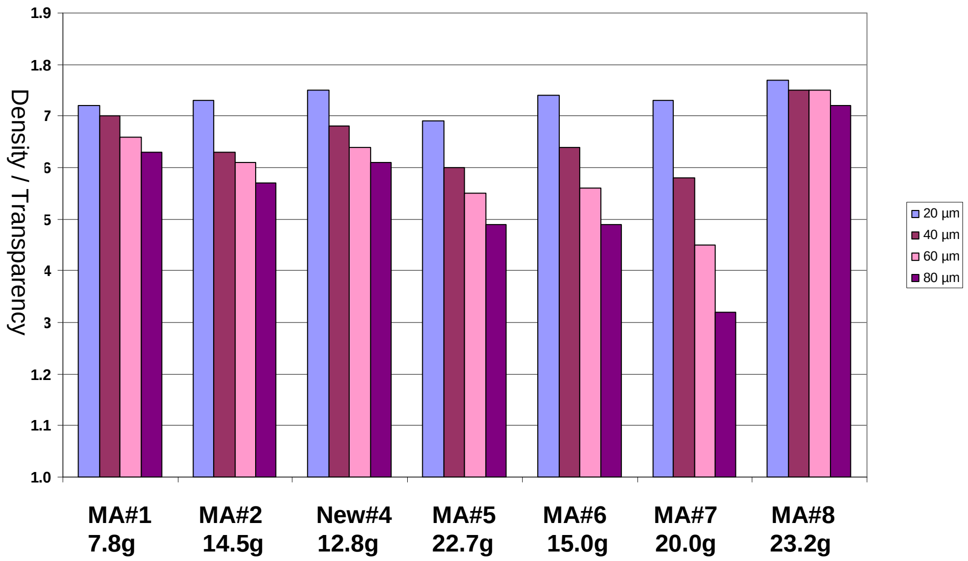
fine matting agent – high layer thickness

Another critical factor in matting UV coatings is the influence to viscosity build-up which results with some grades, mainly due to the higher loading needed to reduce gloss down to a very matte finish. Higher viscosity build has detrimental effects to application and overall appearance. In this study, slide 11 reviews behavior of the eight products tested. The New #4 grade introduced demonstrates the least influence and after the very low shear rate of 1 sec^{-1}, viscosity behavior is close to being Newtonian, in the range from 10-1000 sec^{-1}.

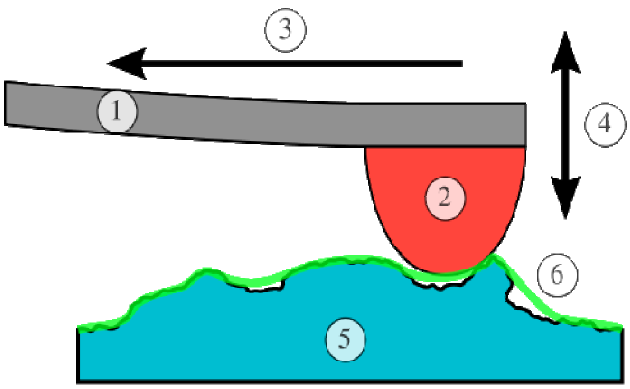


Results pertaining to transparency of cured coatings are reviewed in slides 12 -14. Comparisons were made at different film thicknesses (20, 40, 60, 80 and 120 microns) and at two different gloss ranges (15@60° and 20@60°). To assess transparency, drawd owns were made over polymethylmethacrylate (PMMA) panels at different film thicknesses. These matted, clear coated panels (with the 8 matting agents tested) were placed over both white and black contrast charts. A densitometer was used to assess transparency. In both cases, transparency was measure over white and black contrast and higher values indicate higher clarity / transparency. [For those not familiar with this type of test to detect transparency, the human eye can typically detect a difference of 0.1.] As expected, when film thickness increases, transparency decreases. With some grades, this difference was very minimal, however, with others the decrease is significant. An overall very good level of transparency was maintained using the NEW grade #4. In this case, MA#8 showed the best performance, over thicknesses from 20-80 microns. This is also an unexpected result, given this grade required a high loading of matting agent to achieve the targeted gloss of 15@60°. A significant reduction in transparency was observed at higher film builds with MA#7.

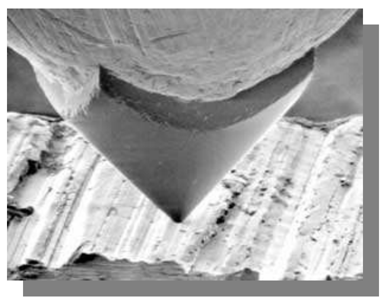
Transparency Comparsion of Gloss 15 @ 60°



Surface roughness performance is summarized in slides 15 – 18, where slide 15 describes the surface roughness measurement contact Profilometer.

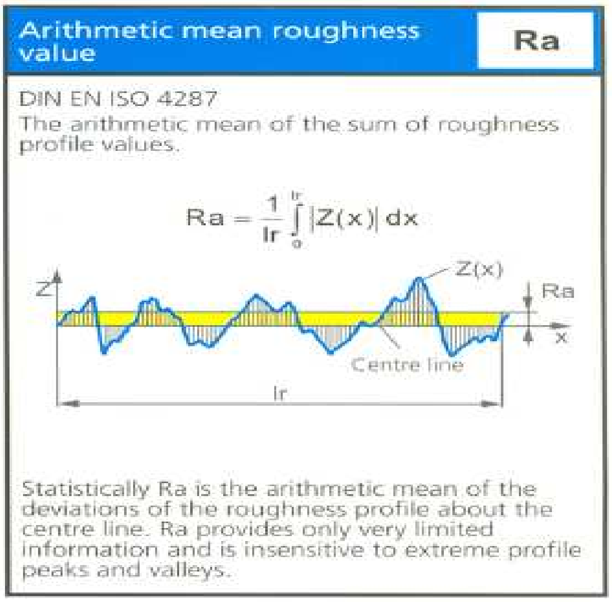


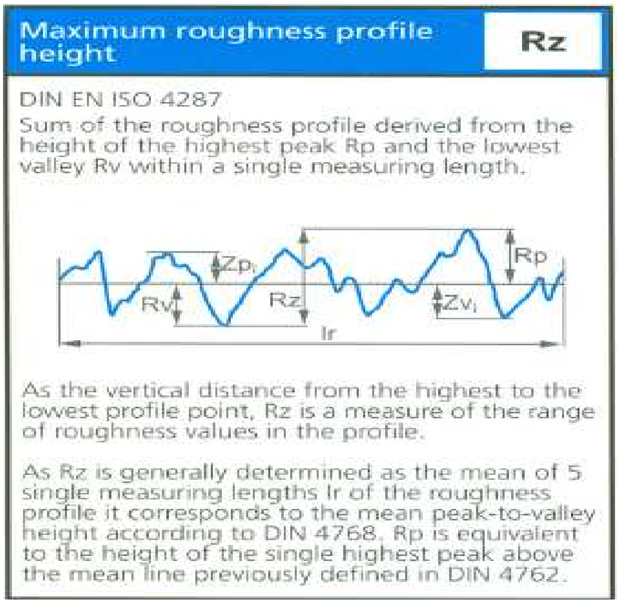
diamond needlepoint (2)



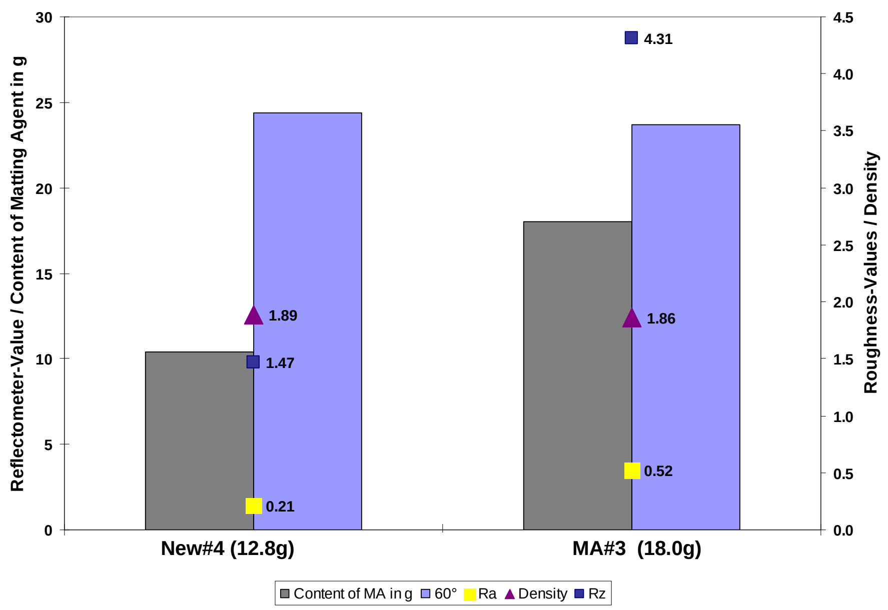
The roughness measurement with contact profile meters is a method for the description of surfaces. During the roughness measurement, a needlepoint from a diamond **(2)** slides over the substrate (work piece) **(5)** with constant speed **(3).** The measuring profile **(6)** is produced by the vertical position shift of the diamond needlepoint **(4),** which is usually converted in an electric signal. As a result, standardized roughness parameters are detected by the electric signals, which can be used for the description of a surface.

The two resulting roughness values which are reported from this measurement are: Ra and Rz. The Ra value is the arithmetic mean roughness value from the absolute value of all profile values of the measuring section. The Rz value indicates the distance from the highest peak to lowest part of the trough. These two values together give a description of the roughness by indicating whether there are few or many peaks (high roughness) and the depth of the peaks (whether they are shallow or deep troughs). The technical definitions of these values are as follows:

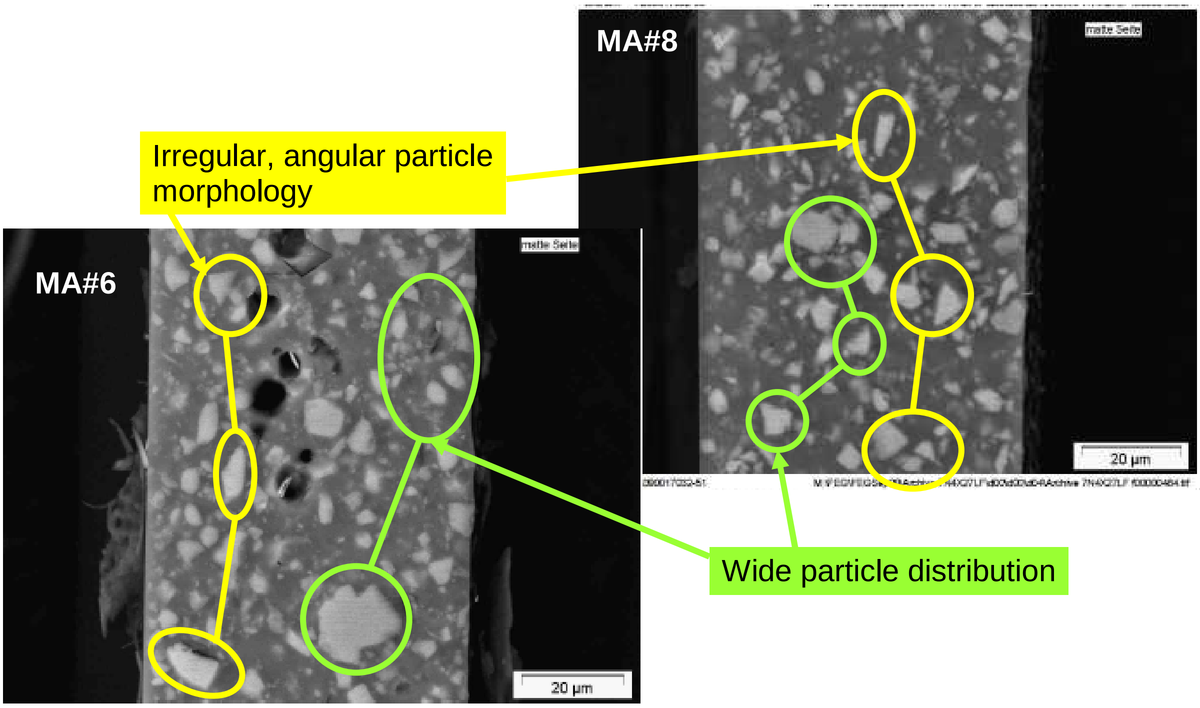


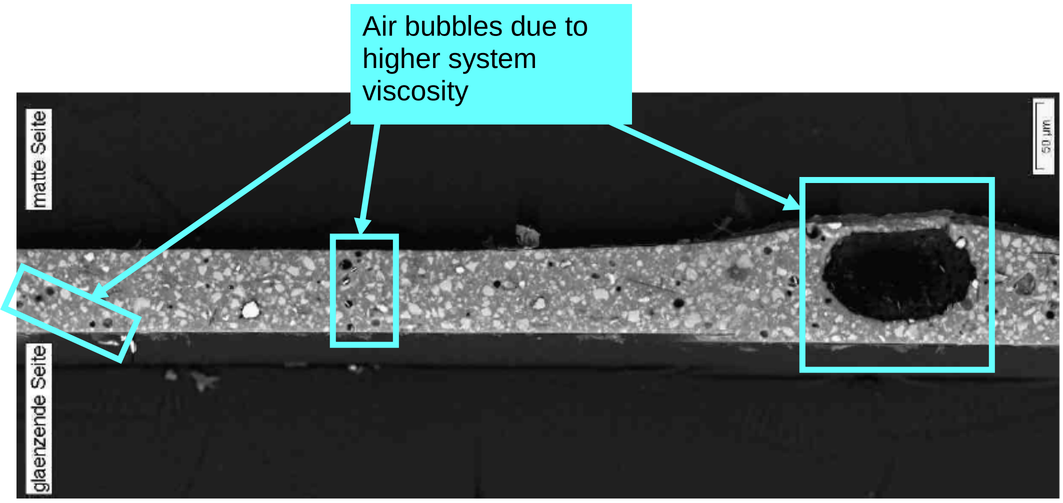


Results show overall (slide 18), the New MA#4 gives a balanced combination of high matting efficiency, with minimal roughness (lower Ra and Rz) values, indicating high surface smoothness with comparable high transparency.

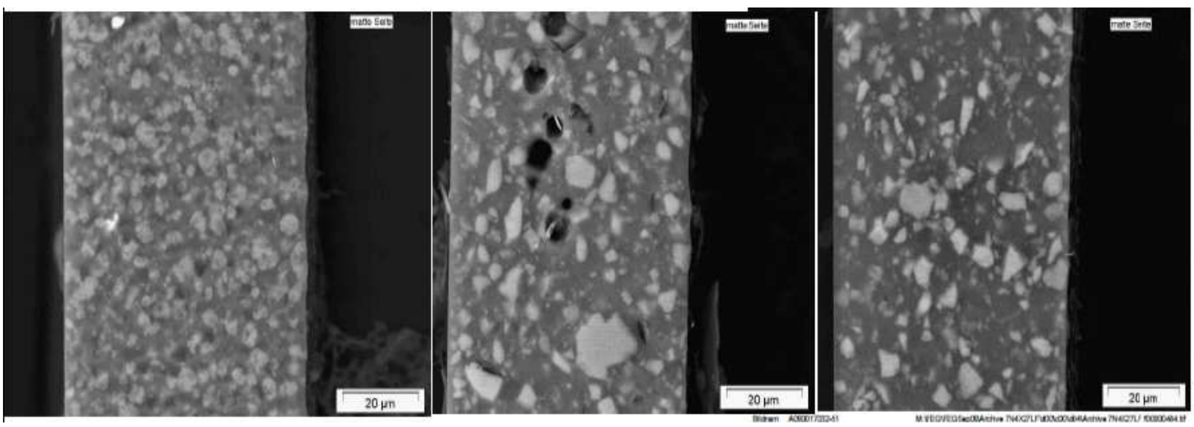


Photomicroscopy summarized in slides 19 – 25 details differences in morphology and particle distributions of the various grades included in this study. SEM analysis shows current technology targeted to matte UV coatings have highly angular and irregular shapes, with wide particle size distributions apparent throughout all SEM analysis. Air bubbles can be easily observed in several cross-sections of UV coatings matted with technology MA#6 and this can be attributed to the higher formulated viscosity encountered to achieve the target gloss level.





SEM Comparison of cross-section cuts of matting coatings:



New MA#4 **MA#6** **MA#8**

In summary, the new reactive siloxane treated, precipitated silica technology represented by MA#4 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.