Novel Matting Agent for Low-Gloss UV Coatings

By Hans-Dieter Christian, Reinhard Behl, Andreas Feller and Maria Nargiello

hile 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 in which 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 specially designed

TABLE 1

Physico-chemical data of products included in study

	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
Туре	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
рН	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

TABLE 2

Formulation used for study

UV Test Coating System	Content (%]	
Oligomer: Aminomodified Polyether Acrylate	77,70	
Monomer: Hexandiol diacrylate	19,40	
Photoinitiator #1: 1-hydroxycyclohexyl benzophenone	2,50	
Photoinitiator #2: Bis(2,4,6-trimethylbenzoyl)- phenylphosphineoxide	0,40	
Total	100,00	

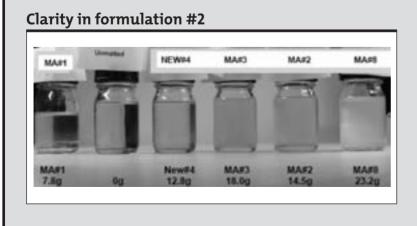
Comparison of loading to achieve gloss of 15 at 60°, 15µm dft Э Į C Marrie MAR2 MART MART MARE MAE7 MARE New#4 MARS 7.8g 14.5g 18.00 12.80 22.70 15.00 20.00 23.20

for low gloss, high transparency and low viscosity was developed for UV coatings.

This article will feature results comparing this new generation of matting agents to the matting technology considered "state-of-theart" in UV applications. The focus will be on gloss versus viscosity behavior. Photomicroscopy based on REM and TEM-Thin-Cut will be used to demonstrate the performance of this unique, new technology.

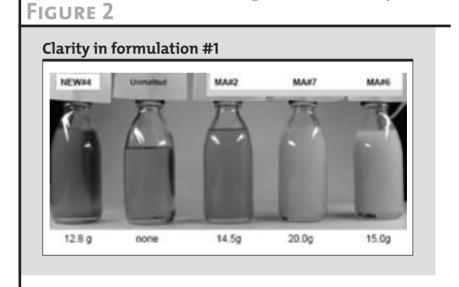
Matting agents or additives to increase surface roughness have evolved over the decades based on a

FIGURE 3



variety of sources, including ground polymeric types to those based on silicon dioxide. This paper will focus on those based on SiO2 from precipitated, fumed 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 New #4 will be compared to those currently available on the market.

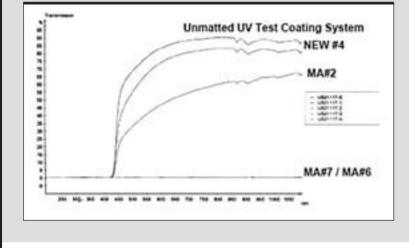
Table 1 outlines typical physicalchemical properties of the matting agents included in the study and then



reviews the formulation used and data pertaining to performance. Values tested include matting efficiency at 60° and 85°, viscosity buildup which is a major consideration in UV coatings, especially when trying to achieve low-gloss finishes in the area of 10 at 60°. Other results presented pertain to transparency, surface smoothness and morphological differences in technology as assessed through Scanning Electron Microscopy(SEM) analysis of films.

NOVEMBER/DECEMBER 2010 RADTECH REPORT 41

UV-Vis comparison of New #4 to technology on the market



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

Matting agents were all added at varying levels to achieve gloss of 15 at 60°. Once the gloss level was fixed; matting efficiency, viscosity buildup and transparency were all assessed. The formulation used for this study is noted in Table 2.

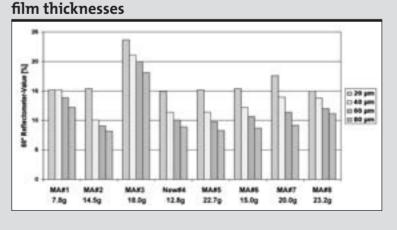
To achieve this gloss range, loadings varied for the eight grades tested from a low level of 7.8g to 23.2g. Matting agent loading levels are noted in grams, on 100g weight formulation. In the case of MA #1, 7.8 grams on 100g formulation was needed to achieve gloss of 15. In the case of MA #8, 23.2 grams on 100g formulation was needed to reduce gloss to 15. 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 higher formulation viscosity encountered presented several application problems that will be highlighted in the SEM analysis later in this article. Figure 1 highlights the comparison of loading differences to achieve the target gloss range.

Clarity in the formulation itself is loading-level dependent; however, it is also a function of the treatment type. Figures 2 and 3 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 New #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. The UV-Vis transmission curve comparison on Figure 4 also illustrates 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.

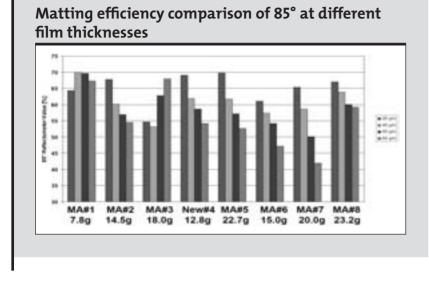
Figures 5 and 6 present the gloss data at 60° and 85° over four different film thicknesses of 20, 40, 60 and 80 microns. Coatings were applied by wire-wound rod to BYK contrast cards No. 2854. Matting efficiency in UV systems is dependent on several factors and certainly the physicalchemical properties 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.

Concerning sequence of addition, matting agents were added and dispersed after photoinitiators were added. They can also be premixed with

FIGURE 5



Matting efficiency comparison of 60° at different film thicknesses



monomers. Typically, dispersants are not suggested, as they could act to reduce matting efficiency.

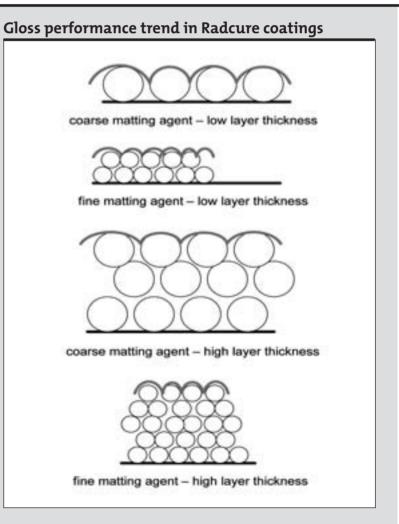
Typically, fast line speed and highly reactive oligomers lead to higher gloss. Slower line speed (allowing for better orientation) combined with the use of lower reactive oligomers will contribute to improved matting. In this system, two different initiators were used, taking advantage of the different sensitivities to the wavelengths. Photoinitiator #1 is used for shorter wavelengths, while Photoinitiator #2 (normally used for pigmented coatings) is specialized for longer wavelengths. In matted clear coatings, Photoinitiator #2 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, synergistic combinations can be found which best suit matting Radcure-based coatings. Examples noted demonstrate such synergistic initiator combinations for thicker films, which was the basis for their selection.

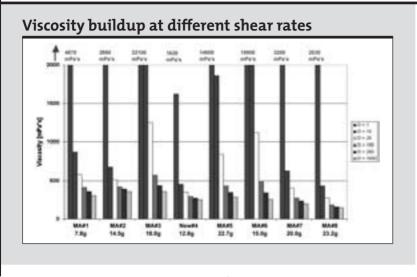
Figure 7 demonstrates an interesting performance trend for matting UV coatings, which differs from matting other types of coatings—

FIGURE 7

it is a behavior that 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 volumeshrinkage 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.

Another critical factor in matting UV coatings is the influence to viscosity buildup that 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 on application and overall appearance. Figure 8 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 to 1,000 sec-1.

Results pertaining to transparency of cured coatings are reviewed in Figures 9-11. Comparisons were made at different film thicknesses (20, 40, 60, 80 and 120 microns)

FIGURE 9

and at two different gloss ranges $(15 \text{ at } 60^{\circ} \text{ and } 20 \text{ at } 60^{\circ})$. To assess transparency, drawdowns were made over polymethylmethacrylate panels at different film thicknesses. These matted, clear-coated panels (with the eight matting agents tested) were placed over both white and black contrast charts. A densitometer was used to assess transparency. In both cases, transparency was measured 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.)

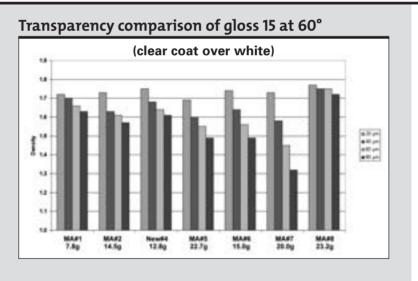
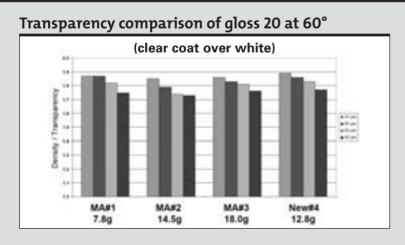
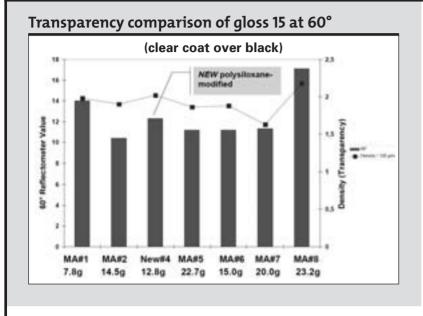


FIGURE 10



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 to 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 at 60°. A significant reduction in

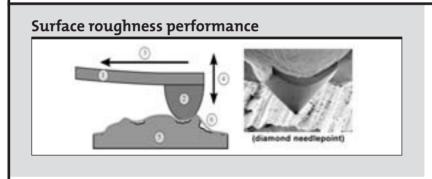


transparency was observed at higher film builds with MA#7.

Surface roughness performance summarized in Figure 12 describes the surface roughness measurement contact Profilometer. The roughness measurement with contact profile meters is a method for the description of surfaces. During the roughness measurement, a needlepoint from a

FIGURE 12

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 that 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



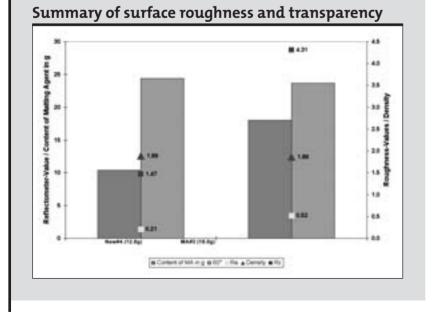


FIGURE 13

indicating whether there are few or many peaks (high roughness) and the depth of the peaks (whether they are shallow or deep troughs).

Results show overall (Figure 13) that 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 Figures 14-16 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

SEM of morphology and particle size distribution (MA#6 and 8)

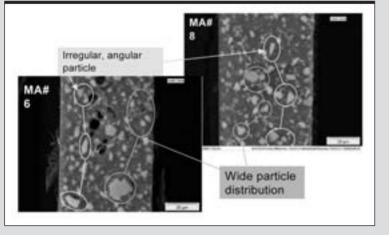


FIGURE 15

SEMs of air bubbles due to high viscosity build

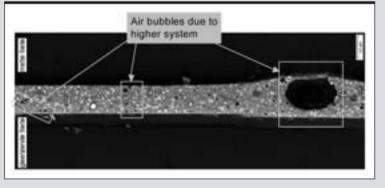
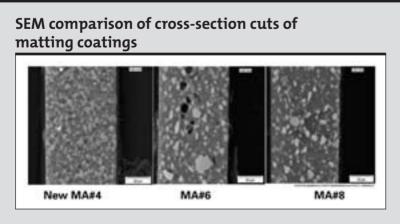


FIGURE 16



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.

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 and transparency, and achieving high surface smoothness.

— Hans-Dieter Christian is a global laboratory manager; Reinhard Behl is a senior laboratory scientist; and Andreas Feller is a senior laboratory scientist for Evonik Degussa Corporation in Wolfgang-Hanau, Germany. Maria Nargiello is a senior technology manager for Evonik Degussa Corporation in Piscataway, N.J.