NEXT GENERATION HIGH EFFICIENT MATTING AGENTS FOR UV COATINGS

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INTRODUCTION

Today’s demands on coating materials in terms of cost efficiency, optimized cycle times and emission of volatile organic compounds (VOC) changed significantly during the last ten years. There are several solutions offered by the industry to match today’s needs on new coating materials. Especially in terms of short cycle times, reduced VOC emissions and outstanding film properties; radiation curable coatings show great potential. This technology offers coating manufacturers the possibility to formulate highly versatile coatings for nearly every field of application.

Compared to conventional coatings (i.e. water borne 1pack or 2pack systems) the field of radiation curable coatings holds different challenges on the formulation and curing side. Many of these challenges are caused by the curing mechanism.

Formulation of matted clear coats can become an extremely tough challenge to the formulator. In case of 100% solid coatings it can be complicated finding the balance between:

- Acceptable viscosity for the targeted application method
- Targeted gloss level
- Desired film properties (e.g. scratch resistance, hardness, chem. resistance, etc.)

THE MATTING MECHANISM

To understand the challenges of matting 100% UV coatings we need to take a look on the classic matting process and compare it to conventional coatings containing volatile compounds.

Due to solvent evaporation, conventional coatings start to orientate and “concentrate” the matting agent during physical drying of the film. As volatile compounds evaporate, the applied film starts to shrink. This shrinkage can vary between 30% up to 60% of the wet films volume depending on volume solids. Compared to this, 100% UV coatings only shrink between 3% and 8% (depends on the used resins and monomers) during the rapid cure cycle.

![Schematic overview about resin / matting agent ratio before and after curing](Picture 1: Schematic overview about resin / matting agent ratio before and after curing)

In case of 100% UV coatings the absence of volatile solvents leads to various problems for the formulator. For lowering the viscosity of the resin and especially in case of higher amounts of matting agents, the use of low viscous monomers is unavoidable. As these monomers will crosslink with the resin they will also influence the final film properties. Lower the gloss targets of
the final coating require more monomer to obtain an acceptable application viscosity. This can lead to reduced film properties, flow and levelling issues, reduced reactivity and other problems. Solvent based systems can overcome this problem due to the thinning ability of the volatile solvents.

Another important factor is the curing speed. Conventional coatings usually show open times between 5 and 30 minutes whereas the curing process of UV coatings takes place in seconds. This small timeframe for cure time in UV coatings prevents an adequate orientation / floating of the matting agents and lowers their efficiency. The result is a much lower efficiency of typical matting agents which needs to be compensated by higher addition rates.

In the following article we have considered a comparison between different classic matting agents (silica and wax based) vs. new approaches for matting UV curable coatings. The main focus of this article is to compare different matting technologies (available and experimental ones) and highlight individual strengths and weaknesses of each technology.

THE CLASSIC MATTING APPROACH

Surface Structuring by Particles
The traditional way of reducing the gloss of a coating is the use of a solid matting agent. In general these matting agents are silica or wax powders. (In many applications, silica is preferred due to its higher efficiency.) Using a classic silica or wax as matting agents means to utilize a particle to add light scattering to the final film. In this approach, the matting agent particles lead to a structured coating surface that does not reflect light directionally anymore. The final structure can vary between fine grain structure and a texture like effect and is influenced by particle size, porosity and chemical nature of the matting agent.

NEW APPROACHES TO ACHIEVE MATTING

Moving away from the classic particle based matting approach means looking for alternative mechanisms to scatter light in a coating film. In this abstract, we will focus on two novel ways to achieve light scattering: Internal Light ScatteringTo obtain low gloss values it is necessary to scatter the light reflected by the film. Most matting approaches focus on scattering the light on the coatings surface. In case of clear coats significant amounts of visible light will pass through the coating film and will be absorbed and reflected by the substrate.
By creating light scattering structures such as defined crystal structures inside the coating film, the light that passes into the film will be scattered inside and the film appears matte. In case of this new matting additive the matting performance is achieved via a controlled crystallization during the curing process. This new additive technology is based on the synergistic effect between an acrylic functional carrier and a special polymeric solid phase. The internal light scattering behaviour can be seen by looking inside the coating with a laser microscope. Inside the coating a refractive pattern similar to caustics in a swimming pool becomes visible. Each of these structures corresponds to a crystalline border in the film. Due to the interaction of the crystals with light the film becomes matte.

B) Surface Structuring (without particles)
By influencing the surface curing of a radiation curable coating the final film can be forced to form a heavily structured layer. This highly “wrinkled” surface scatters the incoming light which can lead to very low gloss values.

One approach to achieve a surface texture without particles is by utilizing special curing equipment such as “Excimer” devices in combination with specially formulated coatings. e will not discuss Excimer equipment in this study but we will focus on a different way to achieve comparable structuring pattern. Structured surface effects can be developed by influencing the surface flow of a coating during the curing process. In case of the used chemistry the single particles cause the coating to flow away from the particles. This flow process is related to polarity changes of the coating during the curing process and generates micro scale waves that appear while the coating cures process.

OVERVIEW OF THE COMPARISONS

In this study we compared the above mentioned matting processes to show specific advantages and disadvantages of each matting process. Emphasis lies on:

A) General efficiency at different use levels
B) Stability of matting effect at various film thicknesses
C) Compatibility with various oligomers

For performing these specific comparisons the following materials were used:

<table>
<thead>
<tr>
<th>Generation #1</th>
<th>Generation #2</th>
<th>Silica</th>
</tr>
</thead>
<tbody>
<tr>
<td>Proprietary blend of polymers</td>
<td>Proprietary blend of polymers</td>
<td>Untreated silica (represents the classic matting approach – can be obtained by wax or silica)</td>
</tr>
<tr>
<td>Main matting mechanism: Internal light scattering</td>
<td>Main matting mechanism: Internal light scattering Surface structuring (without particles)</td>
<td>Main matting mechanism: Surface structuring (particles)</td>
</tr>
<tr>
<td>Mean Particle Size: 6 µm</td>
<td>Mean Particle Size: 9 µm</td>
<td>Mean Particle Size: 9 µm</td>
</tr>
</tbody>
</table>

Table 1: detailed overview of matting agents technologies studied
Due to its high reproducibility and the ease to use all application tests were carried out by using a draw down application on contrast charts. The film thickness is indicated in the different segments individually.

For all microscopic pictures a KEYENCE VK-X210 laser scanning microscope was used. The confocal laser scanning microscopy is suited to analyse surface structure effects at a very high resolution. In addition the technology is able to virtually look into a coating film to determine the internal light scattering behaviour of a coating.

A) GENERAL EFFICIENCY AT DIFFERENT USE LEVELS

As coating viscosity and formulation costs are important drivers for choosing the right Generation #1 Matting Agent setting up the final formulation, the selected matting agents should show a maximum efficiency to keep addition rates at a minimum.

To check the efficiency of the different matting approaches the above mentioned matting agents were incorporated at varying addition rates into a common UV curable coating system based on epoxy- and polyester acrylates. For this test the addition rates varied between

![Graph 1: Gloss development at different addition rates](image)

### Coating formulation “Polyester/Epoxy Acrylic”

<table>
<thead>
<tr>
<th>Raw material</th>
<th>Addition level</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laromer®² LR 9004</td>
<td>40,0</td>
<td>Polyester acrylic</td>
</tr>
<tr>
<td>Laromer®² LR 8986</td>
<td>31,0</td>
<td>Epoxy acrylic</td>
</tr>
<tr>
<td>Laromer®² DPGDA</td>
<td>24,5</td>
<td>Thinning monomer</td>
</tr>
<tr>
<td>Byk®³ A-530</td>
<td>0,5</td>
<td>Air release agent</td>
</tr>
<tr>
<td>Irgacure® ¹ 186</td>
<td>4,0</td>
<td>Photo initiator</td>
</tr>
</tbody>
</table>

¹ Irgacure® is a registered trademark of the BASF Group
² Laromer® is a registered trademark of the BASF Group
³ BYK® is a registered trademark of BYK Chemie
Generation #1 Matting Agent:

Even at low addition rates, the internal light scattering technology of the Gen #1 Matting Agent shows a significant lower gloss compared to a particle based approach. Interestingly the matting efficiency shows a maximum at approximately 5% addition level. After reaching this “maximum efficiency” the matting performance gets worse by increasing the Silica content. This phenomenon is related to the matting approach itself. The internal light scattering is caused by controlled crystal formation in the coating film. By increasing the addition level of the internal light scattering matting additive, the number of crystals increases and the matting performance improves. At a certain point a maximum density of crystalline borders in the film is reached. In this specific system, the point of maximum crystal border density is reached at 5% Silica content. Adding more matting agent to the system forces the crystalline borders to overlap and finally to disturb each other which results in less efficient light scattering – the gloss goes up.

Generation #2 Matting Agent:

This matting agent utilizes a multipurpose approach to reduce the gloss of the final film. The gloss development is comparable to Generation #1 Generation #2 Matting Agent the overall efficiency is higher. This similarity in the matting efficiency at low addition rates between Generation #1 and Generation #2 Matting Agents is related to the internal light scattering. Due to the multi-functional approach by using more than one matting mechanism the gloss increase at higher addition rates is significantly lower compared to Generation #1 Matting Agent. (The loss of performance caused by overlaying crystals can be compensated by surface structuring.) On the microscopic pictures it is visible that at 1% addition level the formation of microscopic “craters” around each particle occurs. This texture effect is related to flow effects that occur during the curing process. The coating around each particle moves away and leaves a small dent with the particle in the center. The size of these dents is approx. 20 – 30µm in diameter and 3-4µm deep. By increasing the amount of matting agent the texture effect is increasingly crowded until it starts to interconnect and form a uniform texture comparable to an Excimer pattern.
Silica:
The particle based approach leads to an almost linear matting curve. The more silica is added to the coating the rougher the surface becomes. This can also be seen by looking at the microscopic pictures taken from the coatings surface. In addition the surface structures obtained with silica tend to be more “rough” with less uniformity and a more irregular height profile compared to the texture obtained by the Generation #2 Matting Agent.

B) STABILITY OF MATTING EFFECT AT VARIOUS FILM THICKNESSES

In the field of UV curable coatings, film thickness is another important topic for discussion. Usually the matting efficiency highly depends on the particle size of the matting agents. In general this means by increasing the particle size of silica the matting efficiency will be improved. This also means that changing the applied film thickness might have a significant influence on the final matting performance.

In this study, the influence of film thickness on the efficiency of the different matting mechanisms will be tested. Therefore the same coating was applied at different film thicknesses.

![Graph 2: Gloss development at different film thickness](image)
As expected the pure particle approach shows an almost linear correlation between film thickness and gloss. By exceeding the mean particle size of the used silica (9µm) the gloss significantly goes up.

On the contrary, the particle approach Generation #1 Matting Agent and Generation #2 Matting Agent show an almost stable performance over all tested film thicknesses. Once a sufficient film thickness is reached for the internal light scattering it does not matter if the film thickness changes. This leads to a very consistent performance over a wide film thickness range.

C-) COMPABILITY TESTS IN VARIOUS OLIBOMERS

Besides the efficiency of a preparation, a broad compatibility is a key criterion for a matting additive. To compare the efficiency of the new matting approaches a broad test series was set up including several acrylic oligomers. The goal behind these trials is to formulate a simple coating and check the compatibility and effectiveness of the subject matting additives in it.

Basic formulation scheme:

<table>
<thead>
<tr>
<th>Oligomer</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oligomer</td>
<td>65.0%</td>
</tr>
<tr>
<td>Irgacure® 1 500</td>
<td>5.0%</td>
</tr>
<tr>
<td>UV Matting Prototype</td>
<td>5.0%</td>
</tr>
<tr>
<td>DPGDA</td>
<td>25.0%</td>
</tr>
</tbody>
</table>

Graph 3: comparison data in different oligomers

Generation #1:
The matting efficiency of Generation #1 Matting Agent correlates with the reactivity of the tested oligomers. As the internal light scattering is based on precipitation processes that occurs while the curing process, the whole matting mechanism is influenced by curing speed and most
importantly on the gel time. It is clearly observable that high reactive systems with short gel times prevent the coordinated formation of the matting crystals.

**Generation #2:**
The combination of different matting mechanisms results in two major advantages: (I) broad compatibility with lower influence by the oligomers reactivity and (II) higher efficiency than pure internal and pure surface light scattering. As a significant portion of the matting performance is still linked to structural and crystalline formations, the oligomers reactivity influences the final matting performance.

**Silica:**
In this study, silica shows consistent performance across the range of most of the tested oligomers. Reactivity is slightly influencing the final matting performance but not as significant compared to Generation #1 and Generation #2 Matting Agents. The matting efficiency of the silica particles is more influenced by wetting and flow properties of the oligomers in the formulation. The final surface roughness that gives the matting efficiency is in most cases almost identical and so is the gloss.

**CONCLUSION**

Utilizing other mechanisms than the traditional ones often means changing the way a formulation is set up to get optimum results. Generation #1 and Generation #2 matting agent technologies developed by Lubrizol Advanced Materials, Inc and reviewed in this study are a first step into developing new approaches to control the light scattering properties of radiation curable coatings.

The data presented in this article indicates that the first and second generation technologies can be used to develop low gloss UV cured coatings. In general, these new technology matting agents using a combination of different matting mechanisms show superior performance at varying film thicknesses and at lower additive levels whereas the surface scattering effects of silica yields consistent and stable matting across a broader range of monomer/oligomer combinations.

<table>
<thead>
<tr>
<th>Pros</th>
<th>Pros</th>
<th>Pros</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Generation #1</strong>&lt;br&gt;Proprietary blend of polymers</td>
<td><strong>Generation #2</strong>&lt;br&gt;Proprietary blend of polymers</td>
<td><strong>Classic matting</strong>&lt;br&gt;Untreated silica (represents the classic matting approach)</td>
</tr>
<tr>
<td>• High matting power at low addition levels&lt;br&gt;• No influence on coating viscosity&lt;br&gt;• Superior surface feel&lt;br&gt;• Mechanical stable matting effect (as the matting appears inside the film it is not polish able)&lt;br&gt;• Uniform matting.</td>
<td>• High matting power at low addition levels&lt;br&gt;• Low influence on coating viscosity (compared to standard silica)&lt;br&gt;• Superior surface feel&lt;br&gt;• Broad compatibility in different oligomers&lt;br&gt;• Very uniform matting with better aesthetics.</td>
<td>• Efficiency develops almost linear – easy and reliable gloss control&lt;br&gt;• Standard matting method with long experience on formulators side</td>
</tr>
<tr>
<td>Cons</td>
<td>No linear correlation between addition level and resulting gloss values</td>
<td>No linear correlation between addition level and resulting gloss values</td>
</tr>
<tr>
<td>------</td>
<td>---------------------------------------------------------------------</td>
<td>---------------------------------------------------------------------</td>
</tr>
<tr>
<td></td>
<td>Ideal addition range varies depending on the formulation details</td>
<td>Efficiency depends on the formulation details (reactivity, curing speed, used raw materials)</td>
</tr>
<tr>
<td></td>
<td>Efficiency depends on the formulation details (reactivity, curing speed, used raw materials)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Limited usability in pigmented systems</td>
<td></td>
</tr>
</tbody>
</table>

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