Water Borne Self-Matting Polyamide Technology

Eric Broz
Coatings Trends & Technologies Conference
September 10, 2019

WHAT WE ADD MAKES THE DIFFERENCE™
TYPICAL POLYURETHANE

\[
\text{Polyol (Soft segment)} + \text{Poly-Isocyanate (Hard segment)} + \text{Acid (Water dispersing)} + \text{Diluent (Viscosity control)}
\]

Polyamide Technology

WHAT WE ADD MAKES THE DIFFERENCE™

© The Lubrizol Corporation 2019, All Rights Reserved.
SEGMENTED POLYMERS – THERMOPLASTIC ELASTOMERS

Segments of **soft blocks** and **hard blocks**

Physical and mechanical properties dependent of segment properties and intermolecular interactions

Common soft segments in PUD are made of **polyester, polyether, or polycarbonate polyols**

Chemical and physical properties strongly influenced by soft segment
Lubrizol has invented a new building block for synthesizing polymers, in particular, new waterborne polyurethane dispersions.

### DIFFERENT TYPES OF POLYOLS – SOFT SEGMENTS IN PUD

<table>
<thead>
<tr>
<th>Polyol Type</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyether polyol</td>
<td>Good hydrolytic stability, Poor UV resistance</td>
</tr>
<tr>
<td>Polyester polyol</td>
<td>Good mechanical properties and UV resistance, Poor hydrolytic stability</td>
</tr>
<tr>
<td>Polycarbonate polyol</td>
<td>Good UV and hydrolytic stability, High price and limited composition variability</td>
</tr>
<tr>
<td>Polyamide polyol</td>
<td>Previously believed to be not suitable for soft segment, no commercial availability</td>
</tr>
</tbody>
</table>

*Diagram showing chemical structures of polyols.*
PROBLEMS WITH POLYAMIDE OLIGOMERS

• Tendency to form crystalline, **high melting**, structures due to strong intermolecular hydrogen bonding

• **Viscosity** usually **too high** to handle in common PUD processes

• Additional synthesis step needed to convert amine or carboxyl chain-ends to hydroxyl (**cost**)

• Raw material **availability**

• Isocyanates may **react** with amide

• **Moisture** hold-up

Many reports on attempts to make polyamide-urethane polymers, but little commercial success so far...
**FUNCTIONAL POLYAMIDES** were developed with amine and/or hydroxyl terminations and controlled:

- Molecular weight
- Hydrophobicity
- Hydrogen bonding
- Branching/rings

**URETHANE WITH A CHEMICALLY INERT SOFT SEGMENT AND VERY HIGH HARD SEGMENT COMPATIBILITY**

**POLYAMIDE based URETHANES are NOT:**

- Impossible to process in any form …
- Water sensitive: swells/blushes at ambient …
- Brittle without any elongation or strength whatsoever …
ADVANTAGES OF POLYAMIDE POLYURETHANE

MECHANICAL & CHEMICAL
- High Hardness
- Excellent Chemical Resistance

ADHESION
- Nylon/Polyamides
- Glass
- Polar surfaces

HYDROLYTIC & THERMAL STABILITY
- Hydrolytic:
  - AMIDE >> ESTER
- Thermal:
  - AMIDE >> ETHER
PERFORMANCE EVALUATION OF URETHANES

Waterborne PUD
Soft Segment Type:

- POLYAMIDE
- POLYCARBONATE
- POLYETHER
- POLYESTER
POLYAMIDE TECHNOLOGY
CURRENT APPLICATIONS

Applications:
• Industrial Metal Coatings
• Wood Coatings
• Masonry Flooring Systems

Features:
• High Hardness
• Excellent Chemical Resistance
• Film Clarity
NWFA – INDUSTRY OUTLOOK
EXPECTED DEMAND – FINISH TYPE

Percentages reflect NWFA Members who anticipate a higher or lower demand for finish types. Source: 2018 NWFA

Current Trend --- Lower Gloss; Natural-Look Coatings for Wood Flooring
TRADITIONAL MATTING TECHNIQUE

• Matte appearance is caused by a reduction in the amount of specular reflected light; this is linked to surface roughness.

• One of the more common techniques of matting uses the addition of large, non-soluble particles to create a micro-texture surface during film formation (i.e. Silica, Kaolin, Bentonite, Waxes).

• Develop resins with very large particles mixed in to create surface roughness and generate topography on the surface.
PRO AND CONS OF TRADITIONAL MATTING ADDITIVES

Wide variety of matting additives allow formulation flexibility for specific applications

Tend to negatively impact performance properties

Soft settling of non-soluble particles leads to stability issues and shelf life constraints

Traditional matting agents are efficient, but have a large opportunity for improvement
IMPACT OF MATTING ADDITIVES ON A TYPICAL RESIN

Using matting additives to lower gloss has a significant NEGATIVE impact on both durability & appearance.

**Gloss**

- 60°: 80, 20
- 85°: 80, 60

**Haze**

- 7X Increase in Haze

**Taber Abrasion**

- 1000 Cycles CS-17 Wheel (mg loss)
- 56% Increase in mg Loss

**Pencil Hardness**

- Decrease in Hardness

3 coats on Maple laminate panels
Formulated to ≤275g/L US VOC
Recommended Applications

- Wood interior applications requiring high performance in a matte finish
- Metal and general topcoat applications needing a flat look with great color saturation

Polymer Physical Characteristics*

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance (wet)</td>
<td>Milky White Dispersion</td>
</tr>
<tr>
<td>Total Solids by Weight, %</td>
<td>35.0 ± 1.0</td>
</tr>
<tr>
<td>Total Solids by Volume, %</td>
<td>34.2 ± 1.0</td>
</tr>
<tr>
<td>Density, lbs./gal (g/ml)</td>
<td>8.69 (1.04)</td>
</tr>
<tr>
<td>Brookfield Viscosity, cps</td>
<td>&lt; 500</td>
</tr>
<tr>
<td>pH</td>
<td>7.5 – 8.5</td>
</tr>
<tr>
<td>Volatile Organic Compounds, wt. %</td>
<td>0.85 TEA</td>
</tr>
<tr>
<td>Freeze-Thaw Stability</td>
<td>Protect from freezing</td>
</tr>
<tr>
<td>NMP, NEP, and APEO-Free</td>
<td></td>
</tr>
<tr>
<td>VOC - Can formulate to &lt;275 g/L (USA) / 110 g/L EU VOC</td>
<td></td>
</tr>
</tbody>
</table>

*Property values represent typical results only and are not to be considered specifications
NEW SELF-MATTING PUD

• As the self-matting coating dries, micro scale viscosity and surface tension abnormalities generate a matted surface
• This resin does NOT contain large particles commonly used to create self matting coatings, leading to improved stability
• This resin can reach a 60° gloss of 16 GU without the use of matting additives (gloss can be reduced further with a small amount of polymeric matting agent)
SELF-MATTING VS. TRADITIONALLY MATTED PUD RESIN

Gloss

Taber Abrasion
1000 Cycles CS-17 Wheel (mg loss)

Haze

Pencil Hardness

Self-matting PUD reaches lower gloss than traditionally matted PUD without sacrificing either durability or appearance

3 coats on Maple laminate panels
Formulated to ≤275g/L US VOC
SELF-MATTING PUD CHEMICAL RESISTANCE

Chemical Resistance on Wood

<table>
<thead>
<tr>
<th></th>
<th>MEK (1hr)</th>
<th>Formula 409 (1hr)</th>
<th>Mustard (1hr)</th>
<th>Water (24hr)</th>
<th>IPA (24hr)</th>
<th>Ketchup (24hr)</th>
<th>Vinegar (24hr)</th>
<th>Old English (24hr)</th>
<th>Grape Juice (24hr)</th>
<th>Hot Coffee (24hr)</th>
<th>Red Wine (24hr)</th>
<th>Windex (24hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Self-matting PUD</td>
<td>√</td>
<td>√</td>
<td>√</td>
<td>√</td>
<td>√</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>√</td>
</tr>
<tr>
<td>High Gloss Commercial Control</td>
<td>√</td>
<td></td>
<td>√</td>
<td>√</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>√</td>
</tr>
<tr>
<td>Low Gloss Commercial Control</td>
<td>√</td>
<td>√</td>
<td>√</td>
<td>√</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>√</td>
</tr>
</tbody>
</table>

MFMA Chemical Resistance (1hr Recovery)

<table>
<thead>
<tr>
<th></th>
<th>DI Water (4hr)</th>
<th>1% Spic N Span (4hr)</th>
<th>Veg Oil (4hr)</th>
<th>50% EtOH/DI water (1hr)</th>
<th>Naphtha (1hr)</th>
<th>Cola (1hr)</th>
<th>Budweiser (1hr)</th>
<th>Perspiration (1hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Self Matting PUD</td>
<td>√</td>
<td>√</td>
<td>√</td>
<td>√</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Self Crosslinking PUD</td>
<td>√</td>
<td>√</td>
<td>√</td>
<td>√</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acrylic #1</td>
<td>√</td>
<td>√</td>
<td>√</td>
<td>√</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acrylic #2</td>
<td></td>
<td>√</td>
<td>√</td>
<td>√</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3 coats on Maple laminate panels Formulated to ≤275g/L US VOC

Self-matting PUD outperforms traditionally matted commercial products and performs on par with high gloss coatings
Self-matting PUD performs significantly better for both hardness and abrasion resistance compared to SB and WB commercial products.
PIGMENTED SELF-MATTING PUD IN A PIGMENTED TOPCOAT

Chemical Resistance in a Metal Topcoat Pigmented System

Impact Resistance ASTM

Pigmenting the self-matting PUD improves chemical and corrosion resistance and maintains color when exposed to UV.
ΔE is under 1.0 after 2000 hours of exposure without the use of weathering agents
ACCELERATED WEATHERING
(XENON ASTM D6695-03B CYCLE 6)

ΔE for Xenon

Yellowing (Δb) in Xenon

Δb is under 0.5 after 2000 hours of exposure without the use of weathering agents
COLOR SATURATION OF SELF-MATTING PUD AS A TOPCOAT

L*=26.01  
\(a^*=0.19\)  
\(b^*=-0.43\)

\(\Delta E=0.56\)

L*=26.56  
\(a^*=0.22\)  
\(b^*=-0.36\)

Clear coat on top of black primer
Self-Mattting PUD with External Crosslinker

Addition of external crosslinker positively impacts black heel and barrier properties.

Black Heel Mark

MFMA Chemical Resistance (Before Recovery)

3 coats on Maple laminate panels
Formulated to ≤275g/L US VOC
FEATURES & BENEFITS

- Formulation flexibility due to less matting additives
- Low gloss without sacrificing properties
- Achieving low gloss in high performance coatings with little to no matting additive
- Simplify manufacturing & reduce raw material cost
FEATURES & BENEFITS

Proven durability to protect high value end use

Forms a hard, tough film with exceptional abrasion resistance

Stain resistance maintains coating appearance in many environments

Superior Chemical Resistance
FEATURES & BENEFITS

Visual appeal of natural color & texture of wood

High clarity in a low gloss formulation

Topcoat preserves vibrant color for a more attractive finish
IN SUMMARY

Waterborne, self-crosslinking, self-matting polyurethane dispersion using patented polyamide polyol technology

• Naturally low gloss (16 GU @ 60°) with no matting additives*
• Exceptional hardness, abrasion, and chemical resistance
• Extremely clear film

*Gloss can be further reduced with small amounts of polymeric matting agent

This technology allows formulators to create coatings with beautiful matte finishes and superior durability and protection; while extending the service life
If I only had one slide.....

NO need to sacrifice performance for matte aesthetics
ACKNOWLEDGEMENTS

Dechant, Amanda
Puckrin, Rebecca
Pafford, Robert
Pajerski, Anthony
Peralta, Miriam
Smith, Ryan
Weiner, Jon
Cremona, Dominic
Skoff, Israel
Erdodi, Gabor
Baron, Steve
Latas, Dan
Donati, Pete
Stanislawcyzk, Vic
Swech, Chris
Schneiders, Larry
Sterne, Nick
Wolfinger, Mark
Questions?

The information contained herein is believed to be reliable, but no representations, guarantees or warranties of any kind are made as to its accuracy, suitability for particular applications or the results to be obtained. The information is based on laboratory work with small scale equipment and does not necessarily indicate end product performance. Because of the variations in methods, conditions and equipment used commercially in processing these materials, no warranties or guarantees are made as to the suitability of the products for the applications disclosed. Full-scale testing and end product performance are the responsibility of the user. Lubrizol Advanced Materials, Inc. shall not be liable for and the customer assumes all risk and liability of any use or handling of any material beyond Lubrizol Advanced Materials, Inc.’s direct control. The SELLER MAKES NO WARRANTIES, EXPRESS OR IMPLIED, INCLUDING, BUT NOT LIMITED TO, THE IMPLIED WARRANTIES OF MERCHANTABILITY AND FITNESS FOR A PARTICULAR PURPOSE. Nothing contained herein is to be considered as permission, recommendation, nor as an inducement to practice any patented invention without permission of the patent owner.