A Contemporary Discussion of Emerging Acid-Catalyzed Melamine Technologies

June 5, 2018
2018 Sink or Swim Symposium
Cleveland Coatings Society

Presented by: Morgan Alexander
King Industries, Inc. Norwalk, CT
I. Overview of Melamine Crosslinking Resins
   i. Types of Amino Crosslinkers
   ii. Chemistry of Melamine Resins

II. Acid Catalysts for Melamine Crosslinkers
    i. Types of Acids used with Melamine Crosslinkers
    ii. Benefits of different Acid Catalysts

III. Acid Catalysts for Trending Markets

IV. Summary
I. Overview of Melamine Crosslinking Resins
Amino Crosslinker Sources

**Melamine**
- Exterior durability
- Chemical resistance

**Urea**
- Fast cure response
- High strength
- Cost Effective

**Glycolurilis**
- UV-resistance
- Less CH₂O release

**Benzoguanamines**
- Toughness
- Flexibility
- Detergent resistance
Melamine Crosslinking Resins

Focus on Two Types

1. Fully Alkylated

- No –NH groups
- No methylol

2. High-Imino

- High –NH content
- Some methylol
Melamine Crosslinking Resins

1. Fully Alkylated
   - **Advantages:**
     - Flexibility
     - Shelf-Life
     - Intercoat Adhesion
   - **Common Applications**
     - General Industrial
     - Automotive
     - Coil Coatings
     - Can Coatings

2. High-Imino
   - **Advantages:**
     - Fast cure
     - High hardness
     - Stain resistance
   - **Common Applications**
     - General Industrial
     - Automotive Basecoat
     - Wood Coatings
     - Plastic Coatings
HMMM
Hexa(methoxymethyl) melamine

Key Points
- Fully methylated crosslinker
- Follows a specific catalysis mechanism ($pK_a$-dependent)
- Best catalyzed with strong acid
High-Imino Melamines

**Key Points**

- High imino (-NH) content
- Some methylol groups
- Follows a **general catalysis mechanism** (not pK$_a$-dependent)

*Catalyzed with strong acid*
*Catalyzed with weak acid*
Reaction Rate vs. pH for Fully Alkylated and High-Imino Melamines

Functional groups on the amino resin dictate acid catalyst choice.

W.J. Blank, J. COAT. TECH, VOL 51, No. 65, 1979
Catalysis of HMMM by Protonation (SN$_2$)

\[
\begin{align*}
\text{Regenerated catalyst } & + \text{ H--A } \rightleftharpoons \text{ N}^+\text{O}^{-}\text{H} \quad \text{HMMM} \\
\text{N}^+\text{O}^{-}\text{H} \quad & + \text{ R$_1$--OH } \rightleftharpoons \text{ N}^+\text{O}^{-}\text{H} \quad + \text{ R--OH} \\
\text{N}^+\text{O}^{-}\text{H} \quad & + \text{ A$^-$ } \rightarrow \text{ N}^+\text{O}^{-}\text{H} \quad + \text{ H--A }
\end{align*}
\]
Protonation of High-NH Melamine at Low Temperatures

When H-A is a stronger acid:

**Neutralization**

\[ \text{NH}_2\text{O} + \text{H}^-\text{A} \rightleftharpoons \text{H}_2\text{O} + \text{NH}_3^+ + \text{A}^- \]

**Protonation**

\[ \text{NH}_2\text{O} + \text{H}^-\text{A} \rightleftharpoons \text{NH}_3\text{O}^+ + \text{A}^- \]
Protonation of High-NH Melamine at Low Temperatures

When H-A is a weaker acid:

Neutralization

Protonation

\[
\text{Neutralization: } \text{NH}_2\text{O}^- + H^-A \rightleftharpoons \text{NH}_2\text{OH}^- + A^- \\
\text{Protonation: } \text{NH}_2\text{O}^- + H^-A \rightleftharpoons H\text{O}^- + \text{NH}_2^+ 
\]
Melamine Self-Condensation

Factors conducive to self-condensation:
High bake temperature
High melamine content
High moisture content
High methylol content
Strong acid catalyst
**Monomeric Melamines (i.e. HMMM)**

- Reaction rate is directly related to $pK_a$ of acid catalyst
- More efficiently catalyzed with strong acids

**Oligomeric/Polymeric Melamine (i.e. High-NH)**

- Reaction rate is not directly related to $pK_a$ of acid catalyst
- Weak acids can catalyze more efficiently, especially at low temperatures
II. Acid Catalysts for Melamine Crosslinkers
**Acid Categories**

**Sulfonic Acids**

- **p-TSA**
  para-Toluene Sulfonic Acid
  \[\text{O=S=O} \quad \text{CH}_3\]

- **DDBSA**
  Dodecylbenzene Sulfonic Acid
  \[\text{C}_{12}\text{H}_{25} \quad \text{O=S=O} \quad \text{OH}\]

- **DNNSA**
  Dinonylnapthalene Sulfonic Acid
  \[\text{C}_{9}\text{H}_{19} \quad \text{H}_{19}\text{C}_{9} \quad \text{SO}_3\text{H}\]

- **DNNDSA**
  Dinonylnapthalene Di-sulfonic Acid
  \[\text{C}_{9}\text{H}_{19} \quad \text{HO}_3\text{S} \quad \text{H}_{19}\text{C}_{9} \quad \text{SO}_3\text{H}\]

**Acid Phosphates**

- \[\text{RO} \quad \text{P} \quad \text{SO}_3\text{H} \quad \text{OH} \quad \text{RO}\]
Sulfonic Acid Use Levels

Based on degree of acidity

<table>
<thead>
<tr>
<th>Acid</th>
<th>Acid Name</th>
<th>Parts</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="p-TSA" /></td>
<td>p-TSA</td>
<td>1.0</td>
</tr>
<tr>
<td><img src="image" alt="DNNDNSA" /></td>
<td>DNNDNSA</td>
<td>1.5</td>
</tr>
<tr>
<td><img src="image" alt="DDBSA" /></td>
<td>DDBSA</td>
<td>1.8</td>
</tr>
<tr>
<td><img src="image" alt="DNNSA" /></td>
<td>DNNSA</td>
<td>2.8</td>
</tr>
</tbody>
</table>
Catalyst Choice based on Crosslinker

**Stronger Acid**
- p-TSA
- DNNDSA
- DDBSA
- DNNSA

**Weaker Acid**
- Phosphates
- Carboxylates

<table>
<thead>
<tr>
<th>Crosslinking Agent</th>
<th>Acid Category</th>
<th>Specific Acids</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Fully alkylated melamine resins</td>
<td><strong>Stronger acids</strong></td>
<td>p-TSA DNNDSA DDBSA DNNSA</td>
</tr>
<tr>
<td>• Urea-Formaldehyde resins</td>
<td></td>
<td></td>
</tr>
<tr>
<td>• Benzoguanamine resins</td>
<td></td>
<td></td>
</tr>
<tr>
<td>• Glycoluril resins</td>
<td></td>
<td></td>
</tr>
<tr>
<td>• High-Imino resins (at low temp.)</td>
<td><strong>Weaker Acids</strong></td>
<td>Phosphates Metal Salts</td>
</tr>
<tr>
<td></td>
<td>pKₐ: 1-3</td>
<td>Carboxylic Acids</td>
</tr>
</tbody>
</table>
Strong vs. Weak Acid Catalysts
In a Polyester/High-NH Formulation

Pendulum Hardness at Low/High Temperatures

- 15min/225°F
- 15min/300°F

Straight p-TSA vs. Straight acid phosphate
# Effects of Acid Strength on Film Properties

## Properties

<table>
<thead>
<tr>
<th>Properties</th>
<th>Strong Acid</th>
<th>Weak Acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blistering/Popping</td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td>Color change (w/ overbake)</td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td>Embrittlement/Flexibility</td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td>Hardness/Cure response</td>
<td>✓</td>
<td></td>
</tr>
<tr>
<td>Viscosity Stability</td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td>Wrinkling</td>
<td></td>
<td>✓</td>
</tr>
</tbody>
</table>

✓ Indicates properties are better with that type of acid

- Stronger Acid: p-TSA, DNNDSA, DDBSA, DNNSA
- Weaker Acid: Phosphates
Effects of Acid Hydrophobicity on Film Properties

<table>
<thead>
<tr>
<th>Properties</th>
<th>Hydrophilic</th>
<th>Hydrophobic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adhesion</td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td>Telegraphing</td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td>Substrate wetting/leveling</td>
<td>✓</td>
<td></td>
</tr>
<tr>
<td>Aromatic Solubility (seeding)</td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td>Water Solubility</td>
<td>✓</td>
<td></td>
</tr>
<tr>
<td>Moisture/Detergent Resistance</td>
<td></td>
<td>✓</td>
</tr>
</tbody>
</table>

✓ Indicates properties are better with that type of acid
Acid Hydrophobicity on Corrosion Resistance

More hydrophobic acids

Better moisture and corrosion resistance

p-TSA
More hydrophilic

DNNSA
More hydrophobic
Acid Hydrophobicity on Telegraphing

More hydrophobic acids

Better wetting of contaminated substrates

0.32% p-TSA

0.9% DNNSA
Amine-blocked Sulfonic Acids

Fully alkylated and high-NH melamine resins are reactive under acidic conditions but relatively stable at neutral pH’s.

Neutralizing the acid:
- Provides longer shelf-life
- Less pigment interaction

Catalyst dissociation depends on:
- Amine volatility
- Amine basicity
- Film permeability
- Secondary reactions
Amine-Blocked Acid Catalysts

Viscosity Stability of Amine-Blocked Acids Stored at 50°C

- Over-neutralized p-TSA
- Under-neutralized p-TSA

Ref. #511-73
Covalent-blocked Sulfonic Acids

- Typically requires more heat to liberate acid compared to amine-blocked acids.

Benefits:
- Amine-free
- Lower VOC
- Better moisture resistance
- Less tendency to yellow
- Less tendency to wrinkle
Recent Trends:

» **Waterborne coatings** replacing solventborne

» **Lower temperature cure** to lower energy & production costs

» Shift away from chromium-based corrosion-inhibiting pigments
Catalyst 2500
Amine-blocked Sulfonic acid

Attributes:
- Blocked acid
- Broad solubility
- Light Color

Areas of Use:
- LTC 1K formulations
- SB and WB systems
- Clearcoats

Performance in Coating:
- Excellent cure response
- Excellent viscosity stability
- Good exterior durability

Common Applications:
- Automotive coatings
- Coil coatings
- General Industrial
Catalyst 300
Covalent-blocked Sulfonic acid

**Attributes:**
- Consistent cure during storage
- Hydrophobic acid
- Blocked catalyst

**Areas of Use:**
- Primers w/ anti-corrosive pigments
- DTM applications
- 1K formulations

**Performance in Coating:**
- Excellent moisture and corrosion resistance
- Good adhesion properties
- Less wrinkling

**Common Applications:**
- General Industrial thermoset anti-corrosive primers
- Primers for appliance finishes
- Coil-coating primers
Catalyst 300 Performance
In Combination with Anticorrosive Pigments

![Cure Response after Elevated Temperature Storage Graph]

- **MEK, 2X**
- **Catalyst 300**
- **Straight p-TSA**

Days at 50°C

Ref. Catalyst 300 Flyer
IV. Summary
Summary

» **Overview of Amino Crosslinkers**

» **Focus on melamine-based resins:**
  » Fully alkylated vs. High-imino
  » Mechanisms of catalysis and self-condensation

» **Common Acid Catalysts for Melamine-Crosslinked Systems**
  » Effects of acid strength/hydrophobicity
  » Benefits of using blocked acid catalysts

» **Catalysts for Trending Markets**
Thank you

Cleveland Coatings Society

Ben Carlozzo, SOS Chair

Special thanks to John Florio, Steve Knight, and all my colleagues at King Industries

Questions?