Formulating for Tannin Stain Inhibition

April 23, 2013

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• Tannin staining is the discoloration of a painted surface due to the migration of water soluble Tannins (tannic acids) through the film
• May appear immediately or after prolonged exposure to humid conditions
• Tannins may be more concentrated around high pressure areas (i.e. – nails, strapping marks, knot holes)
Phenolic compounds found in many tree species used commercially.

- Two main categories, Hydrolyzable and Condensed

**Hydrolyzable (HT)**
- i.e. Chestnut, Oak
- Glucose or Gallic acid core
- Hydrolyzed by mild acid or mild bases to yield carbohydrate & phenolic acids

**Condensed (CT)**
- i.e. Pine, Cedar, Merbau
- Flavonoid or catechol core
- Not readily hydrolyzable to simpler molecules
**Tannin Staining**

*Extractables from Wood Products*

- Extractables include tannins, oils, and rosin component
  - Wood color is generally related to tannin content
  - All staining is not caused by tannins

<table>
<thead>
<tr>
<th>Softwoods</th>
<th>%</th>
<th>Hardwoods</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Species</td>
<td>%</td>
<td>Species</td>
<td>%</td>
</tr>
<tr>
<td>Ponderosa Pine</td>
<td>5.9</td>
<td>American Elm</td>
<td>2.1</td>
</tr>
<tr>
<td>White Pine</td>
<td>7.0</td>
<td>Northern Red Oak</td>
<td>4.4</td>
</tr>
<tr>
<td>Redwood</td>
<td>10.8</td>
<td>White Oak</td>
<td>5.4</td>
</tr>
<tr>
<td>Western Red Cedar</td>
<td>15.0</td>
<td>Southern Red Oak</td>
<td>9.6</td>
</tr>
</tbody>
</table>

*Wood/Bark Extractives; 3434Wood; Virginia Tech Department of Chemistry (2000)*
Tannin Staining

Methods of Reducing Tannins:

WOOD CONDITIONING

- Natural ageing and washing with oxidative solution (i.e. Oxalic acid bleaching)

BARRIER PROPERTIES

- Resin structure
  - New developments in modified acrylics mimic the natural binding properties of tannin-lignin and tannin-protein complexes
  - Ionization and solubility of tannins reduced when using cationics which can also mimic tannin-protein binding complexes
Tannins (tannic acids) are high molecular weight polyphenolic molecules found in wood – Lignins, Cellulose, and Hemicellulose
### CHELATION

- Multivalent ions combine multiple water soluble tannins of lower $M_w$ to create large complexes that are no longer water soluble.

<table>
<thead>
<tr>
<th></th>
<th>Powder</th>
<th>Liquid</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cations</strong></td>
<td>Aluminum Barium Antimony</td>
<td>Aluminum Zirconium</td>
</tr>
<tr>
<td><strong>pH</strong></td>
<td>7.3</td>
<td>9.5</td>
</tr>
<tr>
<td><strong>Oil Absorption</strong></td>
<td>38.8</td>
<td>35.4</td>
</tr>
<tr>
<td><strong>% Water Solubility</strong></td>
<td>0.17</td>
<td>0.11</td>
</tr>
<tr>
<td><strong>Density g/ml</strong></td>
<td>2.77</td>
<td>3.10</td>
</tr>
<tr>
<td><strong>Mean particle size μm</strong></td>
<td>5.1</td>
<td>3.1</td>
</tr>
</tbody>
</table>
The chelation process is essentially the reaction of slightly water soluble metal cations from inhibitive pigments with hydroxyl groups on the phenolic rings present in all Tannins.
Coalescing Agents

- Ester Alcohols (i.e. Texanol) and Propylene Glycol are preferred.
  - Increased H bonding results in increased effective $M_w$ and decreased mobility

- Glycol Ethers (i.e. Propylene Glycol Monobutyl ether) reduce tannin stain inhibitor efficiency.

Lewis Base $\rightarrow$ Complexed metal ion rendered *unavailable*

\[ \text{R}_1\text{O}^- \quad \text{M}^+ \quad \text{R}_2\text{O}^- \quad \text{R} \]
Formulation & Reformulation

- Tropical wood contains more Condensed Tannins
  - Bleaching agents has minimal impact
  - Require higher loading of Tannin Inhibitive Pigments

- Temperate wood contains more Hydrolyzable Tannins
  - More likely to bleed after initial coating
  - $M_w$ of the tannins can change over time increasing mobility
  - Blends of multivalent ions shown to be more effective
• pH control of the coating can significantly impact the ionization of hydrolyzable tannins
  • Low pH powder Tannin Stain Inhibitors can be used in mildly basic coating formulations
  • High pH liquid Tannin Stain Inhibitors can replace neutralizing agents and buffers in formulations to effectively limit tannin mobility

• Zinc containing Tannins Stain Inhibitors can reduce the dependency of Zinc oxide in wood coatings
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Jessica Olmos – Project Chemist