Tert-Butyl Acetate: VOC-Exempt Solvent for Coatings
Outline

- Solvent Use in Coatings
- Solvent Regulations
- Tert-Butyl Acetate as a VOC replacement
  - TBAC properties
  - Formulating compliant products with TBAC
    - Lacquers
    - Urethanes
    - Epoxies
    - Alkyds
- Conclusions
Solvent Uses in Coatings and Adhesives

- Resin Synthesis
  - Acrylics, alkyds
- Formulation
  - Resin solubilization
  - Pigment grinding
- Surface Preparation
  - Parts degreasing
- Application
  - Viscosity reduction
  - Surface wetting
  - Flow and leveling
  - Hardness development and curing
- Cleanup
  - Spray gun cleanup
Solvent Regulations Multiply…

- **International Regulations**
  - Montreal protocol on ozone depleting substances (ODS)

- **National Regulations**
  - Control of Volatile Organic Compounds (VOCs)
  - Control of Hazardous Air Pollutants (HAPs)

- **State and local regulations**

- **Grass roots initiatives**
Grass Roots: Green Building Initiatives

- EPA lacks jurisdiction to regulate indoor air quality
- Health and environmental concerns:
  - Indoor air quality (VOCs, HAPs, ozone, PM, mold, pollen, etc…)
  - Materials safety (lead, asbestos, phthalates)
  - Efficient use of resources (energy and materials)
  - Environmental impact of products (global warming, pollution, ozone depletion)
- Leading to new product certification requirements:
  - Leadership in Energy and Environmental Design (LEED rating)
  - Green Seal product standards:
    - Commercial Adhesives (GS-36)
    - Paints and Coatings (GS-11)
    - Stains and Finishes (GS-47)
Benefits of “Greener” Solvents

• Protect the environment, worker and consumer

• Reduce product liability

• Avoid impact of regulations

• Extend product life

• Expand markets and sales

• Promote a positive company image
Why Regulate VOCs in Coatings?

- Volatile Organic Compounds (VOCs) contribute to ground level ozone (smog) formation
- Ozone is a lung irritant and criteria pollutant
- Major sources (biogenic, cars and truck) are difficult to reduce
- Coating operations are a minor but visible source of VOCs
- Low-VOC coating technologies exist
  - Water-based
  - Energy curable (UV and powder)
  - High solids
  - Exempt solvents
VOC Regulations in the US and Canada

- US lowers ozone standard to 75 ppb in 2008
- Effective 9/30/09, TBAC is VOC-exempt in Canada for architectural and automotive coatings
- US and Canadian Regulations based on photochemical reactivity
  - Only photochemically reactive compounds are regulated
  - Negligibly reactive compounds are exempt:
    - Acetone, methyl acetate, TBAC, many halogenated solvents.
    - Many halogenated compounds are regulated under the Montreal protocol because they deplete stratospheric ozone.
Reactivity of Solvents Varies Greatly

Replacing reactive solvents with exempt solvents reduces smog from coating emissions

Based on Dr. William Carter’s SAPRC-99 model
http://pah.cert.ucr.edu/~carter/reactdat.htm
Formulating with TBAC

• TBAC is a medium-fast evaporating solvent (2.8 times n-BuAc)
• Solvent blend must contain ~30% slow solvent for optimum flow, leveling and appearance (e.g. MAK, EEP, PMA, xylene)
• TBAC blush resistance superior to acetone and methyl acetate
• Slow solvents should be used for pigment grinding
• TBAC can be used with isocyanates and amido curatives
• TBAC is stable in acid-catalyzed varnishes
• Coating properties are unaffected because TBAC evaporates first
Resins Soluble in TBAC

- Acrylics and styrene acrylics
- Urethanes and isocyanates
- Alkyds and polyesters
- Modified alkyds (silicone, oil-modified urethanes, acrylic and phenolic)
- Nitrocellulose and other cellulosic resins
- Some chlorinated resins (not PVC)
- Epoxies and their amino and amido-amine curatives
- Melamine and urea-formaldehyde
- Phenolic and styrenated
- Silicones and silanes
Coating Applications

• Coatings – Solvent-based
  – Automotive refinish clearcoats
  – Industrial maintenance coatings
  – Wood lacquers and enamels
  – Aerospace coatings
  – Metal coatings
  – Concrete coatings
  – Traffic paints

• Resin solvent: alkyds, acrylic resins

• Spray equipment cleanup, thinners, degreasers
# Wood Lacquer Reformulations

<table>
<thead>
<tr>
<th>Components</th>
<th>Conventional Formulation</th>
<th>TBAc/n-BuAc Formulation</th>
<th>TBAc/PMAc Formulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>RS 1/2 Nitrocellulose</td>
<td>14.3</td>
<td>14.3</td>
<td>14.3</td>
</tr>
<tr>
<td>Beckosol 12-035</td>
<td>11.7</td>
<td>11.7</td>
<td>11.7</td>
</tr>
<tr>
<td>Diisononyl phthalate</td>
<td>3.0</td>
<td>3.0</td>
<td>3.0</td>
</tr>
<tr>
<td>xylene</td>
<td>30.5</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>MEK</td>
<td>10.7</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>n-butyl acetate</td>
<td>22.7</td>
<td>13.9</td>
<td>13.9</td>
</tr>
<tr>
<td>n-butanol</td>
<td>7.1</td>
<td>7.1</td>
<td>7.1</td>
</tr>
<tr>
<td>PM Acetate</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>TBAc Solvent</td>
<td>0.0</td>
<td>50.0</td>
<td>50.0</td>
</tr>
<tr>
<td>Total lbs</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
</tr>
<tr>
<td>lbs VOC/lb solids*</td>
<td>3.99</td>
<td></td>
<td>1.50</td>
</tr>
<tr>
<td>lbs HAP/lb solids</td>
<td>2.29</td>
<td></td>
<td>0.23</td>
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<tr>
<td>Viscosity, cps</td>
<td>146</td>
<td>185</td>
<td>102</td>
</tr>
<tr>
<td>Dry Time, min</td>
<td>20</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>20 degree gloss</td>
<td>42</td>
<td>47</td>
<td>49</td>
</tr>
<tr>
<td>60 degree gloss</td>
<td>86</td>
<td>87</td>
<td>89</td>
</tr>
<tr>
<td>Whiteness index</td>
<td>65</td>
<td>67</td>
<td>67</td>
</tr>
<tr>
<td>Yellowness index</td>
<td>6.0</td>
<td>5.4</td>
<td>5.4</td>
</tr>
</tbody>
</table>

**Replaced xylene, MEK, and BuAc with TBAC and PMA**

**Lower HAPs & VOCs**

**Dry time is reduced/coating properties unchanged**

Beckosol® is a registered trademark of Reichhold Chemical.
# 2K Urethane Clearcoat Formulations

<table>
<thead>
<tr>
<th>Components</th>
<th>Conventional</th>
<th>TBAC-Based</th>
<th>Conventional High-solids</th>
<th>TBAC-Based</th>
</tr>
</thead>
<tbody>
<tr>
<td>G-Cure 105 P70</td>
<td>100.0</td>
<td>100.0</td>
<td>50.0</td>
<td>50.0</td>
</tr>
<tr>
<td>JONCRYL 920</td>
<td>0.0</td>
<td>0.0</td>
<td>50.0</td>
<td>50.0</td>
</tr>
<tr>
<td>T-12 (1% in toluene)</td>
<td>1.9</td>
<td>1.9</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>FC 430 (10% in toluene)</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>HDI Trimer</td>
<td>28.3</td>
<td>28.3</td>
<td>33.9</td>
<td>25.4</td>
</tr>
<tr>
<td>IPDI Trimer</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>15.6</td>
</tr>
<tr>
<td>MAK</td>
<td>25.0</td>
<td>25.0</td>
<td>24.0</td>
<td>24.0</td>
</tr>
<tr>
<td>n-Butyl acetate</td>
<td>25.0</td>
<td>0.0</td>
<td>24.0</td>
<td>0.0</td>
</tr>
<tr>
<td>TBAc Solvent</td>
<td>0.0</td>
<td>25.0</td>
<td>0.0</td>
<td>24.0</td>
</tr>
<tr>
<td>Total lbs</td>
<td>205.5</td>
<td>205.5</td>
<td>206.5</td>
<td>213.6</td>
</tr>
<tr>
<td>% solids</td>
<td>46%</td>
<td>46%</td>
<td>51%</td>
<td>51%</td>
</tr>
<tr>
<td>lbs VOC/gal*</td>
<td>4.40</td>
<td>3.28</td>
<td>3.96</td>
<td>2.86</td>
</tr>
</tbody>
</table>

- Significant VOC reductions are possible

G-Cure® is a registered trademark of the Cognis Corporation  
JONCRYL® is a registered trademark of Johnson Polymers (BASF)
2K Urethane Clearcoat Properties

<table>
<thead>
<tr>
<th>Properties</th>
<th>Conventional</th>
<th>TBAC-Based</th>
<th>High-solids</th>
<th>TBAC-Based</th>
</tr>
</thead>
<tbody>
<tr>
<td>lbs VOC/gal*</td>
<td>4.40</td>
<td>3.28</td>
<td>3.96</td>
<td>2.86</td>
</tr>
<tr>
<td>Viscosity, sec #2 Zahn</td>
<td>21.2</td>
<td>21.1</td>
<td>20.9</td>
<td>20.8</td>
</tr>
<tr>
<td>Dry Time, hours</td>
<td>3.2</td>
<td>3.5</td>
<td>7</td>
<td>4</td>
</tr>
<tr>
<td>20 degree gloss</td>
<td>88</td>
<td>88</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>60 degree gloss</td>
<td>95</td>
<td>95</td>
<td>95</td>
<td>95</td>
</tr>
<tr>
<td>DOI</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>Reverse Impact, lbs</td>
<td>160</td>
<td>160</td>
<td>160</td>
<td>160</td>
</tr>
<tr>
<td>Direct Impact, lbs</td>
<td>160</td>
<td>160</td>
<td>160</td>
<td>160</td>
</tr>
<tr>
<td>Cross hatch adhesion, %</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
</tr>
<tr>
<td>10% acid resistance (30 min)</td>
<td>pass</td>
<td>pass</td>
<td>pass</td>
<td>pass</td>
</tr>
<tr>
<td>100 MEK double rubs</td>
<td>pass</td>
<td>pass</td>
<td>pass</td>
<td>pass</td>
</tr>
</tbody>
</table>

- No change in coating performance
TBAC: Not Your Typical Ester Solvent

• Other esters react with amino and amido epoxy curatives

• Studied four types of amine and amido curatives

• Compared stability in xylene, TBAC, n-Butyl acetate

• Accelerated aging at 60°C for 30 days
  — Equivalent to one year at ambient temperature

• Measured residual amine using ASTM D2896
Storage Stability of Amine and Amido Curatives

- Xylene and TBAC show similar stability

Ancamide and Ancamine are trademarks of Air Products & Chemicals.
2K Epoxy Reformulation

<table>
<thead>
<tr>
<th></th>
<th>Xylene Formulation</th>
<th>TBAC Formulation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Part A</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Epon 1001X75</td>
<td>301</td>
<td>301</td>
</tr>
<tr>
<td>Pigment &amp; fillers</td>
<td>260</td>
<td>260</td>
</tr>
<tr>
<td>Beetle 216-8</td>
<td>12</td>
<td>12</td>
</tr>
<tr>
<td>Xylene</td>
<td>221</td>
<td></td>
</tr>
<tr>
<td>Aromatic 100</td>
<td></td>
<td>30</td>
</tr>
<tr>
<td>ARCOSOLV PM</td>
<td></td>
<td>76</td>
</tr>
<tr>
<td>TBAC Solvent</td>
<td></td>
<td>115</td>
</tr>
<tr>
<td>MAK</td>
<td></td>
<td>15</td>
</tr>
</tbody>
</table>

| **Part B**          |                    |                  |
| Epicure 3115        | 131                | 131              |
| Xylene              | 70                 |                  |
| Aromatic 100        |                    | 15               |
| TBAC Solvent        |                    | 55               |

**Formulation constants**

- Volume Ratio A/B: 75/25 75/25
- Wt % Solids mixed: 62 62

Non-HAP Solvents
Effect on HAP and VOC Contents

- **Xylene Formulation**
  - HAP Content: 3.87 pounds per gallon
  - VOC Content: 0.84 pounds per gallon

- **TBAC Formulation**
  - HAP Content: 3.87 pounds per gallon
  - VOC Content: 2.79 pounds per gallon
# Epoxy Coating Properties

<table>
<thead>
<tr>
<th></th>
<th>Xylene Formulation</th>
<th>TBAC Formulation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Film Properties after 7 days</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thickness, mils</td>
<td>1.93</td>
<td>1.94</td>
</tr>
<tr>
<td>Direct Impact, in.lb</td>
<td>160</td>
<td>160</td>
</tr>
<tr>
<td>Reverse Impact, in.lb</td>
<td>160</td>
<td>160</td>
</tr>
<tr>
<td>Crosshatch adhesion</td>
<td>100%</td>
<td>100%</td>
</tr>
<tr>
<td>1/8 Mandrel bend pass</td>
<td>pass</td>
<td>pass</td>
</tr>
<tr>
<td>800 hours Salt Spray</td>
<td>&lt;1 mm creep</td>
<td>&lt;1 mm creep</td>
</tr>
<tr>
<td>ASTM B117</td>
<td>7 VF blisters</td>
<td>7 VF blisters</td>
</tr>
</tbody>
</table>

Cure speed & film properties were identical
Other Coating Uses for TBAC

- Alkyd coatings for general industrial and decorative coatings
- Conversion varnishes for wood
- Resin suppliers now offering alkyd resins in TBAC:
  - Reichhold, CCP, Hexion, Nuplex
- Acrylic polyols in TBAC also available from:
  - CCP, Cognis, Rohm & Haas, BASF (Johnson Polymer)
Clear Catalyzed Conversion Varnish

- Used on kitchen cabinets, furniture and flooring
- Resin System:
  - Coconut alkyd: Beckosol® 12035-E2 (65% NV in 32/4 TBAC/A100)
  - Polyol: SAA-100 (100% NV)
  - Crosslinker: Cymel U80 (98% NV)
- Solvents used:
  - TBAC, n-butanol, MAK
  - Small amounts of Aromatic 100 and Isopropanol
- Varnish formulation
  - 209 grams VOC/L
  - 50wt% solids
  - Viscosity = 75 Cps
- Varnish applied to unprimed oak boards

Beckosol® is a registered trademark of Reichhold Chemical
Cymel® is a registered trademark of Cytec Industries
**White Alkyd Enamel Paint***

- Used on wood trim, cabinets, walls
- Resin System:
  - Soy alkyd: Beckosol® 11081-E2 (70% NV in 26/4 TBAC/A100)
- White pigment: TiO$_2$
- Solvents used:
  - TBAC/mineral spirits 26/10, 2% methanol
- Enamel properties
  - 250 grams VOC/L
  - 62 wt% solids
  - Viscosity = 68 KU
  - PVC: 21%
  - Pigment to binder weight ratio: 0.93
- Enamel applied to unprimed gypsum wallboard

*Enamel paint prepared by Jeff Danneman, Reichhold Chemical.
TBAC Indoor Air Concentrations After Painting

- Model classroom parameters:
  - Room volume 231 m³
  - Area painted: walls = 94.6 m²; flooring = 89.2 m²
  - Air exchange rate = 0.9 hr⁻¹
- Conversion varnish on floor (960 sf)
  - TBAC concentration safe (below acute RfC) after 24 hours
  - TBAC below odor detection threshold after 200 hours (8.3 days)
- White enamel on walls (1,018 sf)
  - TBAC concentration safe (below acute RfC) after 5 hours
  - TBAC below odor detection threshold within a week
TVOCs and Formaldehyde in Classroom @14 Days

- Both paints qualify for LEED credits EQ 3.2 and EQ 4.2
Conclusions

• Coating VOC regulations are spreading and becoming stricter

• VOC-exempt solvents like TBAC are useful formulating tools for cost-effective, high performance coatings

• TBAC is suitable for a wide range of coating technologies

• Solvent-based coatings require less energy to produce, apply, and cure than other low-VOC coatings

• Solvent-based coatings with TBAC can meet stringent VOC-content limits as well as qualify for green building environmental credits