an Environmentally Friendly Blowing Agent for Polyurethane Foams
What is ecomate®?

• A liquid blowing agent or a foam expansion agent
• Is an alternative to replace 141b for rigid and flexible applications
• Has similar properties as 141b
• Is cost competitive & economical
• Meets USEPA regulatory standards as an alternative in PU foams
• RoHS and WEE Compliant
• Been in Commercial use since the past 10 years
### Properties & Comparison

- **Well-suited Blowing Agent for PUR & PIR foams**
- **Similar to HCFC-141b**
  - BP nearly identical: [31.5°C]
  - LFL slightly lower: [5% vs. 7.6 volume%]
  - When blended into polyols – Flammability is a non issue!
  - Solubility stronger with ecomate
- **Not a Drop-In for all systems**
  - Requires Optimization like any other Blowing Agent

#### Properties

<table>
<thead>
<tr>
<th>Properties</th>
<th>ecomate®</th>
<th>141b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiling Point °C</td>
<td>31.5</td>
<td>32</td>
</tr>
<tr>
<td>Gas Lambda Value @ 25°C</td>
<td>10.7</td>
<td>10</td>
</tr>
<tr>
<td>Molecular Weight</td>
<td>60</td>
<td>117</td>
</tr>
<tr>
<td>Specific Gravity</td>
<td>0.982</td>
<td>1.24</td>
</tr>
<tr>
<td>Flash Point</td>
<td>-32 °C</td>
<td>ND</td>
</tr>
<tr>
<td>LEL (ppm)</td>
<td>50,000</td>
<td>72,000</td>
</tr>
<tr>
<td>Ozone Depletion Potential</td>
<td>0</td>
<td>0.11</td>
</tr>
<tr>
<td>Global Warming Potential</td>
<td>~ 1</td>
<td>725</td>
</tr>
</tbody>
</table>
**ecomate® Applications**

- **Rigid Foams**
  - Pour-In-Place Rigid Insulating Foams
  - Commercial Foodservice Equipment/ Commercial Refrigeration
  - Discontinuous Panels
    - Cold Stores
    - Houses – Modular
    - Transport
  - Continuous Panels
    - Flex Faced
    - Metal Faced
  - Block Foams
    - Sheets
    - Pipe Sections
  - Spray Foams
    - Industrial
    - Dwellings
**Applications**

- **Flexible Foams**
  - Integral Skin Foams
    - Automotive
    - Furniture
    - Leisure/Toys
    - Medicinal Applications

- **Flexible Molded Foams**
  - Hypersoft Foams
  - HR Foams
  - Viscoelastic Foams

- **Slabstock Foams**
  - Continuous process
  - Box foaming process
Ecomate® growth

- Healthy growth pattern
- 1 Kilo of ecomate approximately reduces 2 kilo of 141bn
- Climate impact – reduction of over 180 K tons of CO₂ eq.
- Attributed to awareness of ecomate technology
Usage By Application

- Rigid Foams
- Flexible
- Integral Skin
- XPS
Case Study: Discontinuous Panels

- Foaming trials were conducted in Italy at a large equipment supplier.
- Ecomate systems were used and standard densities were obtained as with a 141b system.
- Results:

<table>
<thead>
<tr>
<th></th>
<th>Compressive Strength</th>
<th>Closed Cell Content</th>
<th>K-Value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>180 kPa</td>
<td>&gt;95%</td>
<td>0.023W/mK</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Panel</th>
<th>Nominal Density</th>
<th>Core Density</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Left Side</td>
</tr>
<tr>
<td>Panel “a”</td>
<td>40 kg/m³</td>
<td>34.35 kg/m³</td>
</tr>
<tr>
<td>Panel “b”</td>
<td>42.5 kg/m³</td>
<td>39.27 kg/m³</td>
</tr>
</tbody>
</table>
Case Study – Continuous Lamination

• Paper Faced foams were run at various thicknesses

• Sole ecomate® and ecomate® with Pentane blends were trialed

• Normal line speeds were maintained – per industry standard

• PUR & PIR systems were trialed on the same line

• Blend results were disclosed at CPI 2012
## Case Study – Continuous Panels

### Results

<table>
<thead>
<tr>
<th>Tests</th>
<th>Sample 1 A</th>
<th>Sample 1B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flame Spread</td>
<td>~20</td>
<td>~50</td>
</tr>
<tr>
<td>Smoke</td>
<td>~100</td>
<td>~700</td>
</tr>
<tr>
<td>Density (kg/m³) Core</td>
<td>35.4</td>
<td>33.24</td>
</tr>
<tr>
<td>Density (kg/m³) Overall</td>
<td>39.3</td>
<td>37.5</td>
</tr>
<tr>
<td>Compressive Strength Kpa (parallel)</td>
<td>213</td>
<td>270</td>
</tr>
<tr>
<td>Compressive Strength Kpa (perpendicular)</td>
<td>166</td>
<td>124</td>
</tr>
<tr>
<td>Dimensional Stability - @ 70°C %vol change</td>
<td>2.2</td>
<td>1.7</td>
</tr>
<tr>
<td>Dimensional Stability - @ (-) 40°C</td>
<td>3.5</td>
<td>0.1</td>
</tr>
<tr>
<td>Dimensional Stability - @ 70°C &gt;90 % RH</td>
<td>6.6</td>
<td>6.4</td>
</tr>
<tr>
<td>Initial k factor (mW/mK)</td>
<td>20.88</td>
<td>21.15</td>
</tr>
<tr>
<td>Aged &gt; 6 months (mW/mK)</td>
<td>23.82</td>
<td>24.78</td>
</tr>
</tbody>
</table>
Laminator Cont.

Ran similar trials at other facilities -

• Blends based on 100% APP for PIR
• Blends based on APP and Sucrose for PUR applications
• Facings used metal (Steel, Zn Al) Flexible Facings (paper & foil)
• Index ~ 300 for PIR (standard catalyst package used)
• Index ~ 120 -150 for PUR
Case Study: Spray Foam (Egypt)

Similar spray trials have been conducted in Mexico, Jamaica, Brazil, the Philippines, South Africa and others.

Trial Run with Eco-spray R-3000:

- Excellent and fine cell structure.
- Foam density 32 - 42g/l {2pcf - 2.6pcf}
- λ- Value was 0.0226 W/mK
- Compressive Strength 42g/l foam was 235 kPa (parallel to rise)
- Dimensional stability 32 and 42 g/l, no measurable change @ -25°C
- Typical Sprayed thickness 100 - 250mm
Case Study: Spray Foam (Mexico)

<table>
<thead>
<tr>
<th>Density/(Kg/m³)</th>
<th>1”</th>
<th>2”</th>
<th>3”</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Core</td>
<td>31.58</td>
<td>32.51</td>
<td>34.58</td>
<td>32.89</td>
</tr>
<tr>
<td>Overall</td>
<td>34.59</td>
<td>38.13</td>
<td>42.27</td>
<td>38.33</td>
</tr>
<tr>
<td>Fk (BTU-in/hr-ft³-°F)</td>
<td>0.1527</td>
<td>0.1644</td>
<td>0.1587</td>
<td>0.1586</td>
</tr>
</tbody>
</table>

**Dimensional Stability**

<table>
<thead>
<tr>
<th>Temperature</th>
<th>70°C (15 days)</th>
<th>No change</th>
<th>No change</th>
<th>No change</th>
<th>No change</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-19°C (15 days)</td>
<td>No change</td>
<td>No change</td>
<td>No change</td>
<td>No change</td>
</tr>
</tbody>
</table>
Stored Systems in Drums/Totes

< 22% LEL
0-5 cm above bung
@ 30-32°C

22% LEL
within drum headspace
Ecomate concentrations were measured at the spray operators as well as in the immediate vicinity. The results indicate that ecomate concentration was below the recommended limit (250mg/m³).

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Methyl Format Concentration</th>
<th>Actual Flow Rate</th>
<th>Period of Sampling</th>
<th>Person/Area Sampled</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.1 mg/m³</td>
<td>65.8 ml/min</td>
<td>12:00-12:50</td>
<td>Spray Operator</td>
</tr>
<tr>
<td>2</td>
<td>1.6 mg/m³</td>
<td>70.3 ml/min</td>
<td>12:03-12:50</td>
<td>Assistant</td>
</tr>
<tr>
<td>3</td>
<td>4.8 mg/m³</td>
<td>71.3 ml/min</td>
<td>12:05-12:50</td>
<td>Static Sample on Center Pole</td>
</tr>
</tbody>
</table>
ecomate® Emissions – Spray 3rd Party Testing

Spray Foam Example:

• ecomate® - emissions were recorded while spray job was in progress

• The emissions were collected where the concentration was expected to be the highest.

• Results:
  ‣ At the gun head: 10 - 12 PPM
  ‣ Over fresh rising foam: 20 - 23 PPM
  ‣ OSHA regulations: 100 PPM
UNDP Validation Report

For neither HCFC-141b nor methyl formate will the LFL be even remotely approached under standard process conditions (ambient temperatures 15-40°C; substance emissions under legal exposure limits), as shown by the following:

Methyl Formate
- LEL = 5% in air by volume = 125 g/m$^3$ = 50,000 ppm
- Maximum concentration allowed by OSHA.NIOSH/ACGIH:
  - TWA = 100 ppm = 250 mg/m$^3$ = 0.20% of LFL
  - STEL = 150 ppm = 375 mg/m$^3$ = 0.30% of LFL

HCFC-141b
- LEL = 7.4% in air by volume = 925 g/m$^3$ = 193,000 ppm
- Maximum concentration allowed (WEEL):
  - TWA = 500 ppm = 2.4 g/m$^3$ = 0.26% of LFL
  - STEL = 3,000 ppm = 14.4 g/m$^3$ = 1.56% of LFL

Conclusions
- Methyl formate as a pure liquid is very flammable and requires proper safeguards. The risk of explosion is, however, remote because of its low heat of combustion.
- A PU system based on methyl formate can be formulated as a low combustible liquid and will not reach the LFL even in the drum’s head space.
- There is no reason to treat methyl formate differently than HCFC-141b.
Things to consider

Ecomate is not a drop in Replacement to 141b

- Needs Optimization like any other Blowing Agent
- Solubility Stronger than 141b
- Slightly Stronger Solvency over 141b
  - 141b has a slightly stronger solvency over R 11
- Is an ester – can hydrolyze (SLOW)
- Slightly more Flammable
  - Only in neat/pure form (LFL 50,000 ppm)
  - In polyols can be treated similar to 141b
Overcoming Challenges

• Optimization
  ‣ Two Steps
    - Shorten the cross link density of the polymer or increase the functionality of the blend
    - Change of surfactant. It affects:
      ◦ Foam Density: Cell Structure
      ◦ Thermal Properties: Shelf Stability
      ◦ Flammability: K Value

<table>
<thead>
<tr>
<th>Table 1a</th>
<th>POLYOLS</th>
<th>OH#</th>
<th>fn</th>
<th>EqWt</th>
<th>Mn</th>
<th>AMT</th>
<th>avg fn</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS2352</td>
<td>240</td>
<td>2</td>
<td>233.8</td>
<td>467.5</td>
<td>50%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R315x</td>
<td>315</td>
<td>3.2</td>
<td>178.1</td>
<td>569.9</td>
<td>50%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Voranol</td>
<td>360</td>
<td>4.5</td>
<td>155.8</td>
<td>728</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2.54

<table>
<thead>
<tr>
<th>Table 1b</th>
<th>POLYOLS</th>
<th>OH#</th>
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<tr>
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<tr>
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<td></td>
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</table>

3.09
Overcoming Challenges

- **Hydrolysis** –
  - Can be inhibited & Catalyst package can be protected

- **Flammability** -
  - Once blended into polyol; Blends are classified **COMBUSTIBLE/ NON FLAMMABLE**
    - Similar to 141b systems
    - Can be transported without Flammable labels (similar to 141b)
  - FSI can help you with engineering expertise & advise you!
  - Shared with Customers against NDA
Processing - Recommendations

TRANSFER (Pressure) - Use Nitrogen not Air. Closed loop transfer recommended with ecomate® in neat form

PUMPS – for Metering - Brass/SS pumps with PTFE/EPDM diaphragms. Gear pumps do not work well due to low viscosity of ecomate®. Electric grounding for transfer as ecomate® vapor can be flammable during transfer

SEALS - PTFE & Kalrez seals recommended, EPDM

METERING - SS turbine flow-meters with tungsten carbide bearings

HOSES - Convoluted Stainless Steel hoses with SS braiding

PIPING – SS with Stainless compression fittings, valves SS with Teflon seals

STORAGE- Steel drums in covered area i.e. Protection from rain and sun
Blending & Drumming Recommendations

**BATCH BLENDING**

- Injected from drums by pumps through check valve to prevent back flow
  - In-situ blending with inline static mixer prior drumming
  - Introduce ecomate® to other ingredients in the bottom of tank with agitation N₂ blanket on blending preferred
  - Pre-blend ecomate® in a major polyol stream and pumped into mixing vessel.

**DRUMMING**

- Formulations should be designed that ecomate® content in polyol is ≤ 6%
- This ensures that blend is not flammable
- Anticipated flash point or the blend should be verified
- Preferred ecomate® content in isocyanate should be below 2%
**ecomate® Pros / Cons**

<table>
<thead>
<tr>
<th>ADVANTAGES</th>
<th>DISADVANTAGES</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Liquid at room temperature</td>
<td>• Not as well known in market</td>
</tr>
<tr>
<td>• Safe to use</td>
<td>• No “household” name behind the technology</td>
</tr>
<tr>
<td>• Thermally efficient</td>
<td>• Has 10 less years in the market than HCs</td>
</tr>
<tr>
<td>• Environmentally benign</td>
<td>• False and misleading rumors</td>
</tr>
<tr>
<td>• Economically advantageous</td>
<td></td>
</tr>
<tr>
<td>• Good end product properties</td>
<td></td>
</tr>
<tr>
<td>• Can replace HCFCs, HFCs, HC’s, and HFOs</td>
<td></td>
</tr>
<tr>
<td>• Worldwide patent position</td>
<td></td>
</tr>
<tr>
<td>• GRAS approval</td>
<td></td>
</tr>
</tbody>
</table>
Conclusions

• Ecomate® foams have fine cell structures
  ‣ More compatibilizing than other Blowing Agents
  ‣ Stronger solvent than other Blowing Agents

• Optimization is recommended for success
  ‣ Increasing the functionality of polyol blend
  ‣ Changing the surfactant type and amount
    - Not all surfactants are created equal
Availability – Brazil
DUFRIIO refrigeração

Available Worldwide

Ecomate® Usage - systems and blowing agent