PHYSICAL BLOWING AGENTS

FOR PU / PIR FOAMS –
A SHORT HISTORY
PHYSICAL BLOWING AGENTS

More than you wanted to know!
Topics

- Jargon
- Types of Blowing Agents
- How they work
- Requirements
- Nomenclature
- History
- Blowing Agent choices
- Thermal Conductivity
- The Future - Blends
JARGON

- **HC** : Hydrocarbon
- **CFC** : Chloro Fluoro Carbon
- **HCFC** : Hydro Chloro Fluoro Carbon
- **HFC** : Hydro Fluoro Carbon

- **ODP** : Ozone Depletion Potential
- **GWP** : Global Warming Potential
- **VOC** : Volatile Organic Compound
Types of Blowing Agents

- **Chemical**
  - Give off Gas with Chemical Rxn or Decomposition $\rightarrow$ CO$_2$ or N$_2$

- **Physical**
  - Boiling Point at or near RT
  - Expand with heat
How Physical BAs Work

- Low Boiling Liquid
  - Soluble in Raws
  - Insoluble in Foam
- Heat ➔ Foam Exotherm
  - SURFACTANT & CATALYSTS
- POOF! FOAM
BA Requirements

What makes a good BA?

- Low Boiling Liquid [ > RT ]
- Efficient Cost Structure
  - Molecular Weight - Low to Moderate
- Solubility
  - in PU ingredients
  - None in PU polymer
- Zero ODP, Zero GWP, non-VOC
- Flammability – Low to None
- Good Thermal Properties
Nomenclature
– DuPont System

- $C_{n-1} \ H_{n+1} \ F_n$
- CFC-11: TrichloroFluoroMethane - $CCl_3F$
  - $C = 1 \ 1-1 \ 0$
  - $H = 0 \ 0+1 \ 1$
  - $F = 1 \ 1 \ 1$
Nomenclature – DuPont System

- \( C_{n-1} \ H_{n+1} \ F_n \)
- **CFC-11**: TrichloroFluoroMethane - \( \text{CCl}_3\text{F} \)
  - \( C = 1 \quad 1-1 \quad 0 \)
  - \( H = 0 \quad 0+1 \quad 1 \)
  - \( F = 1 \quad 1 \quad 1 \)
- **HCFC-22**: ChloroDifluoroMethane - \( \text{CHClIF}_2 \)
  - \( C = 1 \quad 1-1 \quad 0 \)
  - \( H = 1 \quad 1+1 \quad 2 \)
  - \( F = 2 \quad 2 \quad 2 \)
METHANE SERIES

HFCs

HCFCs

CFCs
METHANE SERIES

LIQUIDS

GASES

FLAMMABLE
134 eh?

- HFC-134a
  - \( C_{n-1} \, H_{n+1} \, F_n \)
  - C=2, H=2, F=4
- Therefore, \( C_2H_2F_4 \)
  - CHF_2 – CHF_2 \( \equiv 134 \)
  - CH_2F – CF_3 \( \equiv 134a \)
- The highest symmetry gets the lowest name!
HISTORY

- First Blowing Agent – Water
- Organic solvents – Flammability
- Chlorinated Solvents – Hi BPts, Solvency
- Dupont Refrigerants
  - R11  BPtr>RT  POUR
  - R12, R22  BPtr<RT  FROTH
Blowing Agent - Environmental Characteristics

- ecomate is an attractive long term environmental option

<table>
<thead>
<tr>
<th></th>
<th>ODP</th>
<th>GWP</th>
<th>VOC</th>
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<tbody>
<tr>
<td>CFC 11</td>
<td>1</td>
<td>4000</td>
<td>0</td>
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<tr>
<td>HCFC 141b</td>
<td>0.1</td>
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<td>HCFC 22</td>
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<td>HCFC 124</td>
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<td>2000</td>
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<tr>
<td>HFC 134a</td>
<td>0</td>
<td>1300</td>
<td>0</td>
</tr>
<tr>
<td>HFC 245fa</td>
<td>0</td>
<td>790</td>
<td>0</td>
</tr>
<tr>
<td>Cyclopentane</td>
<td>0</td>
<td>11</td>
<td>YES</td>
</tr>
<tr>
<td>ecomate</td>
<td>0</td>
<td>0</td>
<td>0</td>
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</tbody>
</table>
HISTORY

- **CFCs** – ChloroFluoroCarbons
  - R11 : CCl$_3$F    R12 : CCl$_2$F$_2$
  - **BANNED FROM SALE IN US 1998**

- **HCFCs** – HydroChloroFluoroCarbons
  - R141b : CH$_3$CCl$_2$F
  - **BANNED FROM SALE IN US 2004, USE 2005**

- **HFCs** - HydroFluoroCarbons
  - R134a, R245fa

- **HFOs** – HydroFluoroOlefins - pending
  - 1336mzz-Z    1233zd-E
HISTORY

- **HCs** — HydroCarbons
  - Back on scene
  - PENTANES — nC5, iC5, cC5
- **WATER**
  - Used in Packaging, & Foams > 4 pcf
  - Co-Blow w Others for Cost
- **Ecomate**
  - New kid on Block
**Ecomate** [METHYL FORMATE]

\[
\text{H} - \underset{\text{O}}{\text{C}} - \underset{\text{O}}{\text{CH}_3}
\]

\[
\text{C}_2\text{H}_4\text{O}_2
\]

✓ BP 32 °C
✓ LAMBDA = 10.7 @25°C
✓ GWP = 0
✓ ODP = 0
✓ MW = 60
<table>
<thead>
<tr>
<th>Blowing Agent</th>
<th>$/lb *</th>
<th>Mol Wt</th>
<th>Factor</th>
<th>$/mole</th>
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<tbody>
<tr>
<td>HCFC-141b</td>
<td>**</td>
<td>117</td>
<td>1.00</td>
<td>Ref</td>
</tr>
<tr>
<td>HCFC-22</td>
<td>**</td>
<td>86.5</td>
<td>0.74</td>
<td>-25%</td>
</tr>
<tr>
<td>HFC-245fa</td>
<td>*****</td>
<td>134</td>
<td>1.15</td>
<td>+350%</td>
</tr>
<tr>
<td>HFC-134a</td>
<td>***</td>
<td>102</td>
<td>0.87</td>
<td>+70%</td>
</tr>
<tr>
<td>cC5</td>
<td>**</td>
<td>70</td>
<td>0.60</td>
<td>-45%</td>
</tr>
<tr>
<td>nC5</td>
<td>*</td>
<td>72</td>
<td>0.62</td>
<td>-70%</td>
</tr>
<tr>
<td>ecomate®</td>
<td>*</td>
<td>60</td>
<td>0.51</td>
<td>-65%</td>
</tr>
</tbody>
</table>
Understanding Insulation

- **Thermal Conductivity** – the ability to resist heat/cold transfer or flow.

- Expressed as:
  - **K-factor** [BTU-in/ft²hr°F], or
  - **Lambda** [mW/m⁰K]
  - It is **independent of thickness**

- The **lower** the K-Factor, the **better** the insulation.
## INSULATION

### THERMAL PROPERTIES

- Each Generation was poorer than the last

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<thead>
<tr>
<th>Physical Blowing Agent</th>
<th>Thermal Conductivity</th>
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<tbody>
<tr>
<td></td>
<td>Gas Lambda</td>
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<tr>
<td>CFC-11</td>
<td>8</td>
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<tr>
<td>HCFC-141b</td>
<td>10</td>
</tr>
<tr>
<td>HFC-245fa</td>
<td>12</td>
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</tbody>
</table>

- Each Generation was **more Costly**!
## Current & Past BAs

<table>
<thead>
<tr>
<th>BLOWING AGT</th>
<th>GAS</th>
<th>LAMBDA</th>
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</thead>
<tbody>
<tr>
<td><strong>CFC-11</strong></td>
<td>8</td>
<td></td>
</tr>
<tr>
<td><strong>HCFC-141b</strong></td>
<td>10</td>
<td></td>
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<tr>
<td>HFC-134a</td>
<td>13</td>
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<tr>
<td><strong>HFC-365mfc</strong></td>
<td>10.6</td>
<td></td>
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<tr>
<td>HFC-245fa</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>ECOMATE</td>
<td>10.7</td>
<td></td>
</tr>
<tr>
<td>WATER [ CO₂ ]</td>
<td>16</td>
<td></td>
</tr>
<tr>
<td>HC-nC5</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>HC-iC5</td>
<td>14</td>
<td></td>
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<tr>
<td>HC-cC5</td>
<td>12</td>
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# Properties of PURE Physical BLOWING AGENTS

<table>
<thead>
<tr>
<th>Ecomate®</th>
<th>MF</th>
<th>ML</th>
<th>iC5</th>
<th>nC5</th>
<th>sC5</th>
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<tbody>
<tr>
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<td><img src="image" alt="Structure" /></td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td></td>
<td>C2H4O2</td>
<td>C5H12</td>
<td>C5H10</td>
<td>C3H8O2</td>
<td>C5H12</td>
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</tbody>
</table>
# Properties of PURE Physical BLOWING AGENTS

<table>
<thead>
<tr>
<th>physical</th>
<th>BA</th>
<th>MF</th>
<th>ML</th>
<th>iC5</th>
<th>nC5</th>
<th>cC5</th>
<th>UNITS</th>
</tr>
</thead>
<tbody>
<tr>
<td>MW</td>
<td>60</td>
<td>76.1</td>
<td>72</td>
<td>72</td>
<td>70</td>
<td>g/mol</td>
<td>Lowest MW – less needed</td>
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</tbody>
</table>

**Ecomate** – Low cost, less needed, more efficient!
### Properties of PURE Physical BLOWING AGENTS

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<thead>
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</tr>
<tr>
<td>BP</td>
<td></td>
<td>32</td>
<td>42.3</td>
<td>28</td>
<td>36</td>
<td>49</td>
<td>°C</td>
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<th>cC5</th>
<th>UNITS</th>
<th>MW</th>
<th>BP</th>
<th>λ_{gas}, at 20 °C</th>
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<td>72</td>
<td>72</td>
<td>70</td>
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<td>11-14</td>
</tr>
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<td>14</td>
</tr>
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<td></td>
<td>72</td>
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<td></td>
<td></td>
<td></td>
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<tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- Lowest MW – less needed
- BP – same as 141b
- Lowest Lambda – more efficient

**Ecomate – Low cost, less needed, more efficient!**
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<thead>
<tr>
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<td>36</td>
<td>49</td>
<td>°C</td>
</tr>
<tr>
<td>$\lambda_{gas}$, at 20 °C</td>
<td>10.7</td>
<td>11-14</td>
<td>14</td>
<td>14</td>
<td>11</td>
<td>mW/m°C</td>
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<tr>
<td>SpGr</td>
<td>0.98</td>
<td>0.86</td>
<td>0.62</td>
<td>0.63</td>
<td>0.75</td>
<td>g/l</td>
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**Ecomate** – Low cost, less needed, more efficient!
## Properties of PURE Physical BLOWING AGENTS

<table>
<thead>
<tr>
<th>environmental</th>
<th>Ecomate (MF)</th>
<th>ML</th>
<th>iC5</th>
<th>nC5</th>
<th>cC5</th>
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<tr>
<td>ODP</td>
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<td>0</td>
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<tr>
<td>GWP</td>
<td>&lt;1.5</td>
<td>&lt;1.5</td>
<td>11</td>
<td>11</td>
<td>11</td>
<td>CO₂=1 Negligible GWP</td>
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<tr>
<td>MIR [Smog]</td>
<td>0.06</td>
<td>0.94</td>
<td>1.45</td>
<td>1.31</td>
<td>2.39</td>
<td>ETHANE=0.28 No SMOG</td>
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Ecomate – more Environmentally Friendly!
Properties of SOME neat Physical BLOWING AGENTS

<table>
<thead>
<tr>
<th>flammability</th>
<th>BA</th>
<th>MF</th>
<th>ML</th>
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<th>nC5</th>
<th>cC5</th>
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<tbody>
<tr>
<td>FLASH Pt</td>
<td>-19</td>
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<td>-51</td>
<td>-49</td>
<td>-37</td>
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Ecomate – Less Hazardous!
Properties of SOME neat Physical BLOWING AGENTS

<table>
<thead>
<tr>
<th>flammability</th>
<th>BA</th>
<th>MF</th>
<th>ML</th>
<th>iC5</th>
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<td>-49</td>
<td>-37</td>
<td>°C</td>
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<tr>
<td></td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td>LESS HAZARD</td>
</tr>
<tr>
<td>LFL</td>
<td></td>
<td>5</td>
<td>1.6</td>
<td>1.4</td>
<td>1.5</td>
<td>1.1</td>
<td>vol%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>LESS HAZARD</td>
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Ecomate – Less Hazardous!
# Properties of SOME neat Physical BLOWING AGENTS

<table>
<thead>
<tr>
<th></th>
<th>BA</th>
<th>MF</th>
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</tr>
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<td>5</td>
<td>1.6</td>
<td>1.4</td>
<td>1.5</td>
<td>1.1</td>
<td></td>
<td>vol%</td>
</tr>
<tr>
<td>% Oxygen</td>
<td>53.3</td>
<td>42.1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
<td>Wt%</td>
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</table>

**Ecomate – Less Hazardous!**
### Properties of SOME neat Physical BLOWING AGENTS

<table>
<thead>
<tr>
<th>Properties</th>
<th>BA</th>
<th>MF</th>
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<th>iC5</th>
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<td>0</td>
<td>0</td>
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<tr>
<td>Electrical</td>
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<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Conductivity</td>
<td>1.92 x 10⁹</td>
<td>?</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td></td>
<td>pS/m</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
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Properties of SOME neat Physical BLOWING AGENTS

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<tr>
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<td>1.5</td>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>Wt%</td>
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<tr>
<td>Electrical Conductivity</td>
<td>1.92</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>pS/m</td>
</tr>
<tr>
<td>Heat of COMBUSTION</td>
<td>16.2</td>
<td>25.1</td>
<td>46.7</td>
<td>49.7</td>
<td>46.9</td>
<td>MJ/g</td>
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</table>

Ecomate – Less Hazardous!
Relative Pressures on Burning

![Graph showing relative pressures on burning with Vol% in Air on the x-axis and Pressure (MJ/g) on the y-axis. The graph includes curves for MF, cC5, ML, and 141b.]
HFOs - Future Stars?

✓ HFCO 1233zd-E [Honeywell Solstice LBA]

✓ BP 19 °C
✓ LAMBDA = ? @25°C
✓ GWP = <7
✓ MW 130
HFOs - Future Stars?

- **HFO 1336mzz-Z** [DuPont’s FEA1100]
  - Z
  - DuPont’s FEA 1100

- **C₄H₂F₆**
  - cis-1,1,1,4,4,4-hexafluoro-2-butene
  - $\text{C}_4\text{H}_2\text{F}_6$

- BP 33 °C
- LAMBDA = 9.7 @25°C
- GWP = 9.4
- MW = 164
The Future - BLENDS

- **CFCs** (1960s)
  - ODP & V Hi GWP
  - Water HCs

- **HCFCs** (1990s)
  - CFC Phase-out
  - Non ODP Hi GWP

- **HFCs** (2000s)
  - HCFC Phase-out
  - Non ODP Lo GWP
  - Water HCs Ecomate

- **OLEFINs, ECOMATE, HCs** (2010s)
  - Non ODP Lo GWP
  - Non VOC
  - BLENDS

- **Montreal Protocol**
  - CFC Phase-out

- **Kyoto Protocol**
  - HCFC Phase-out

**OS & V High GWP**

**OS & V Lo GWP**

**Non OS & V**
Why Blend?

- To Reduce Costs
- To Improve Properties
  - Physical
  - Thermal
  - Performance
- To Find Synergies
Past Blends

- Blends have always been “the norm”
- **CFCs**
  - Liquid CFC-11
    - Blends –w Froth CFC-12 allowed low temp applications
    - Lower thermals - With H₂O
- **HCFCs**
  - 141b – used more water to reduce solubility, shrinkage
Past Blends

- **HFCs**
  - Use still more water to mitigate higher costs
  - 365mfc – used HFC-227ea blends to reduce flammability

- **HCs**
  - Only in controlled environments
  - nC5
    - With iC5 – to improve reaction profile, reduce catalysts
    - With cC5 – to improve thermals
Future Blends

- HFOs
  - HFO 1336mzz-Z [**DuPont’s FEA1100**] → blends
    - Optimize Properties
    - Improve Economics
    - Working with
      - HCs
      - Ecomate
      - Methylal
      - Water
Effect of FEA-1100 Blends
DuPont Data

Lambda (mW/mK) @ 23.9°C

cC5 | iC5 | MF | ML
--- | --- | --- | ---
19.7 | 20.9 | 19.7 | 21.1

neat
FEA blend
Effect of FEA-1100 Blends
DuPont data

Lambda (mW/mK) @ 23.9 °C

- cC5: 19.7
- iC5: 20.9
- MF: 19.7
- ML: 21.1
Benefit of Blends - Refrigeration Foams

### Table:

<table>
<thead>
<tr>
<th>25°C</th>
<th>PURE ECOMATE</th>
<th>ECOMATE HC BLEND</th>
<th>FEA-1100 ECO Blend</th>
</tr>
</thead>
<tbody>
<tr>
<td>08B65</td>
<td>08M12</td>
<td>08M12-2</td>
<td></td>
</tr>
<tr>
<td>Lambda</td>
<td>20.1</td>
<td>20.7</td>
<td>20.6</td>
</tr>
</tbody>
</table>

### Graph:

- Ecomate Blends show Synergy!

- 5.6% savings
- 3.2% savings
- 3.3% savings
- 9% savings
- 7.5% savings
Conclusions

• BA BLENDS have long been with us
  • To improve physical properties:
    • Flow
    • Adhesion
    • Thermal Conductivity
    • Solubility
    • Flammability
  • To improve economics
BLENDS – the new Paradigm

Because there is no “perfect” product

✓ HFOs will be blended also
✓ Blends w Ecomate will be BEST Choice!

Ecomate BLENDS can be:

■ More Thermally Efficient
■ More Environmentally Benign
■ Less Flammable
■ More Economical

■ Because neat ecomate already has these properties!
Thank You for your time!