TITLE:
The Benefits of Optimization in Ecomate® Blown Insulating Foams

AUTHOR(S):
John A. Murphy & David Modray, Foam Supplies, Inc.

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Optimization is essential for urethane systems whenever substantial changes are mandated, such as adopting a new blowing agent. Optimization can be used to improve properties, reduce the number of raw materials or reduce costs [or perhaps several of these goals concurrently]. When a rigid foam system is developed that works reasonable well, optimization usually refers to improving a certain property such as k-factor, dimensional stability, or strength.

Previously we have shown how ecomate blown foams have given equivalent, and often superior properties to formulations blown with more conventional HCFC and HFC blowing agents in various applications, such as pour in place, boardstock, spray and refrigeration. These systems had not been fully optimized.

Switching from one blowing agent to another seldom works well when a “drop in” only approach is taken. This paper will show how a few very minor changes in cross link density and surfactant type/amount will lead to major improvements in foam properties. These enhancements include better thermal properties and often better fire properties, improved dimensional stability and improved shelf life.
The Benefits of Optimization in Ecomate® Blown Insulating Foams

JOHN MURPHY  
Foam Supplies, Inc.  
4387 N. Rider Trail  
Earth City, MO 63045

DAVID MODRAY  
Foam Supplies, Inc.  
4387 N. Rider Trail  
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Optimization is essential for urethane systems whenever substantial changes are mandated, such as adopting a new blowing agent. Optimization can be used to improve properties, reduce the number of raw materials or reduce costs [or perhaps several of these goals concurrently]. When a rigid foam system is developed that works reasonably well, optimization usually refers to improving a certain property such as k-factor, dimensional stability, or strength.

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BACKGROUND:

There will shortly come a day when the HFCs currently being used to blow PUR and PIR foams will be withdrawn from the market because of their GWP contributions. There are several options we now can take: 1) We can wait for the next generation HFO/HFE blowing agents [with their high MWs and equally high costs] with little knowledge of their properties or deficiencies; or 2) we can investigate what is available today [HCs and ecomate], using this interim period to optimize the new BA containing systems to maximize their benefits and mitigate any shortcomings. Acting now will give one more freedom, eliminate panic situations, and it will save money!

Ecomate is well suited for blowing Polyurethane and Polyisocyanurate foams. The advantages of ecomate are many [Table 1]: It has a boiling point [32.0°C] which is almost identical to HCFC-141b [32.2°C], so its vapor pressure at any given temperature is similar. The lower flammable limit is slightly lower [5 volume % (or 50,000 ppm) for ecomate vs. 7.6 volume % for 141b] and, like 141b, when blended into polyols, flammability is usually not an issue.

The solubility of ecomate is also like 141b, but a bit stronger. This allows it to be used like 141b [using all the polyols and additives that were used with 141b].

It is environmentally benign [Zero ODP, minimal GWP, and VOC exempt - meaning it will be the LAST transition you need to make]. It has a very low gas lambda value, so it will produce very thermally efficient foams. And perhaps most appealing, it has the lowest molecular weight [MW] of any current blowing agent [BA] candidate [MW=60], coupled with its low cost [which is independent of petrochemical pricing] makes it one of the most cost efficient candidates on the market. Despite these similarities, ecomate is not a direct ‘drop-in’ BA for 141b, just as 141b was not a direct drop in for CFC-11, nor are HFC-245fa or HCs drop-in replacements for 141b. Each of them required optimization to be useful.
Table 1: Physical Properties of several Physical Blowing Agents for PUR/PIR foams

<table>
<thead>
<tr>
<th>Table 1</th>
<th>ecomate</th>
<th>141b</th>
<th>nC5</th>
<th>365/227</th>
</tr>
</thead>
<tbody>
<tr>
<td>MW</td>
<td>60</td>
<td>117</td>
<td>72</td>
<td>150</td>
</tr>
<tr>
<td>BP, °C</td>
<td>32</td>
<td>32.2</td>
<td>36</td>
<td>30</td>
</tr>
<tr>
<td>Flash Pt, °C</td>
<td>-32</td>
<td>-</td>
<td>-49</td>
<td>-</td>
</tr>
<tr>
<td>LFL, ppm</td>
<td>50000</td>
<td>76000</td>
<td>15000</td>
<td>38000</td>
</tr>
<tr>
<td>Lambda</td>
<td>10.7</td>
<td>10</td>
<td>14</td>
<td>10.7</td>
</tr>
<tr>
<td>ODP</td>
<td>0</td>
<td>0.11</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>GWP</td>
<td>~1</td>
<td>725</td>
<td>11</td>
<td>960</td>
</tr>
<tr>
<td>VOC</td>
<td>exempt</td>
<td>exempt</td>
<td>YES</td>
<td>exempt</td>
</tr>
</tbody>
</table>

While many have very successfully converted their formulations to ecomate, many others have thrown up their hands and walked away after that first ‘drop-in’ evaluation. FSI has been selling ecomate systems for the last decade, and has a large and growing cadre of customers in the US and around the world. We will tell you here how to overcome many impediments to use that you may have uncovered.

OPTIMIZATION:

Optimization is not the first thing that a formulator endeavors to do; his first goal always is to get something that works. After that, an acceptable system will be optimized either initially or over a period of time, in an attempt to get a better product. When a raw material [a blowing agent, for example] change is mandated, the system has already been optimized for the previous raw material. The tendency is to substitute the new raw in place of the current material – as a drop-in substitution because it is an easy fix. If the results are seamless, it is considered a “good” substitute. If any problems occur, many formulators [perhaps most] will throw their hands up and walk away, proclaiming that it doesn’t work!

The amount of diligence given to the replacement process depends on the pressure to make that product work. This pressure can be economic [the new raw is cheaper], property driven [we need a Class 1 foam], or mandated by removal of a previous material from the market [the removal of CFC-11 or HCFC-141b, for example]. Mandated changes are the most onerous because they are perceived as extra work [“Why fix it if it isn’t broke?”], and costly! Repeated mandated changes are even more onerous – because one never gets a good return on investment before the next change is mandated.

Each raw material is different one from the other…they have their advantages as well as their disadvantages. This is true especially of physical blowing agents, be it differences in gas lambda, solubility, boiling point, flammability, molar weight, ODP/GWP, or cost [to name a few]. With all these changes [and with all the differences in properties], one has to weigh carefully how these differences can be handled both in the product, and in the plant infrastructure. So these conversions are not trivial in the least.

The purpose of this paper is to share with the formulator and the decision makers some of the optimization work we have recently done, in order to shorten your learning curve with ecomate, and get you up and running with ecomate more rapidly.
Pros and Cons of Ecomate

First, let us examine the advantages of ecomate:

1. It has the lowest MW of any blowing agent on the market today;
   a. So usage levels to achieve an equivalent density are the lowest.
2. It is the most environmentally friendly blowing agent
   a. ODP zero; GWP negligible; non-VOC
3. Its gas lambda value is very competitive with HFC and HFO/HFE BAs.
   a. Therefore, ecomate blown foams should have very low thermal properties, if optimized.
4. It is miscible with all foam raw materials currently used
   a. Compatible with all current blowing agents
   b. And with most solvents, surfactants and catalysts
5. It is the closest replacement for HCFC 141b
   a. Same BP
   b. Similar solubility
   c. Similar flammability range
6. Because of its excellent solubility, polyol mixtures with ecomate can be shipped and used without flammability placarding.
7. It is the least expensive [on a molar basis] Blowing Agent on the market

Let us also examine ecomate's few constraints [which have all been overcome]:

1. It is an ester, and can therefore hydrolyze!
   a. Hydrolysis can lead to shortened system shelf life
   b. There is a resolution which allows $> 1$ year shelf life in most systems
2. It is slightly more flammable that 141b
   a. Properly blended into polyol, it can be handled conventionally!
3. It is a stronger solvent than 141b.
   a. This can lead to shrinkage if not properly formulated for.
   b. This is the purpose of this paper

With so few impediments, it is a wonder that more people are not turning to ecomate as their blowing agent of choice. We believe that it is because it takes a little effort to optimize a system for this product...but only a little effort, mind you. Let's examine these constraints in greater detail.
HYDROLYSIS:

Hydrolysis takes place slowly as a reverse Fischer esterification shown below (one mole of ester [methyl formate] will react with a mole of water to produce a mole of formic acid).

The aspect of hydrolysis frightens many. But this is the identical hydrolysis that has been recognized for years when using polyester polyols. This same hydrolysis phenomenon occurs when using certain new HFO blowing agents! Some have claimed that MF modifies reactivity and shortens shelf stability because of acid increase. Hydrolysis can lead to a shortened shelf life and corrosion of equipment if not addressed. An obvious solution is to keep this product dry. But when formulating, one often adds water to the formulation, and/or the polyols used generally have some water. FSI has developed and patented techniques that will stabilize ecomate systems far longer than are most conventional systems, up to a year in fact. We openly share this information when our customers sign our NDA [non-disclosure agreement]. We can inhibit the hydrolysis scenario and protect the catalyst package from any hydrolysis effects, should any occur.

FLAMMABILITY:

The plant modifications to handle ecomate can be minimal. Our engineering staff can show you many ways to store and handle this material safely. There are far fewer plant modifications needed to safely use ecomate than are needed to implement HCs. This is because ecomate can be blended into polyols to produce systems that are merely combustible, which means that these systems then can be safely handled conventionally.

DIMENSIONAL INSTABILITY:

This is perhaps the greatest impediment to the use of ecomate by formulators. If the first ‘drop-in’ trials fail, many walk away. We will suggest several options here. Let’s first consider from where your formulations are transitioning, since this could make a difference in what steps you take.

A Transition from 141b: Ecomate is the most nearly similar material on the market to 141b – it has the same boiling point, and nearly the same flammability and solubility. But its MW is about half that of 141b, so only half as much is necessary to achieve equivalent density. However, Ecomate has stronger solvency for urethane raw materials than does HCFC-141b. This implies stronger solvency for the finished foam made with it. In addition, it makes really fine celled foams – so fine in fact that the resulting foams have diminished strength since the resulting cells are so very tiny. So with this double whammy of tiny cells and stronger solvency, what are the options for success? One could increase foam index ~10 points, or increase the water content while decreasing the ecomate content [both of these are easy but add expense]. A third option is reformulation [see below].
Transition from HFCs: Transition from HFCs to ecomate is strongly driven by cost [ecomate requires 40% (= 60 / 150) of the amount of 365mfc, at a much lower cost ( < half ), to blow equivalent density foam] and a desire to make this the FINAL conversion. Ecomate gives nearly equivalent thermal properties, but is still quite a bit better solvent than the HFCs. Since nearly all the HFCs [save 365mfc] are gases at room temperature, ecomate affords easier formulating and handling as well. A slight amount of optimization is necessary here as well – mainly increasing the crosslink density [XLD] of the polyol mixture and adjustment of the surfactant [see below].

Transition from HC: Ecomate is dramatically different from the pentanes. While the MWs of HCs are low, that of ecomate is even lower. And the solubility in the various raw materials is spectacularly better with ecomate. The many things you HAD to do to make HCs work [reformulation] will probably have to be undone. The conversion to a PA ester, to higher amounts of fire retardants, to lower viscosity polyols, and to higher amounts of surfactants to stabilize the system - all may work against you.

The solution here is clearly reformulation: For example – say you are producing HC blown laminate boardstock, and want to improve thermal properties, and become ‘green’. By transitioning to ecomate one can lessen the amount of FRA by about 20-30% [a cost savings], a lower amount of catalyst may be in sight, as well as lessened surfactant levels [up to 75% less]. Most importantly, to achieve optimal properties, one should increase the crosslink density of the polyol blend [as outlined above]. The cost savings of reducing the fire retardant, the surfactant and potentially the catalyst levels, and the lower usage levels of ecomate [not to mention the improved thermal properties from its use] are certainly strong incentives for making this transition.

REFORMULATION: This involves two minor steps – increasing the cross-link density [XLD] of the formulation, and changing the type and amount [lessen] of surfactant used.

ADJUSTING THE CROSS LINK DENSITY of the polyol mixture is fairly straightforward. For instance, increasing the amount of a higher functionality polyol and diminishing the amount of a 2 functional ester, or even replacing a 2 Fn ester with one having a 2.3Fn is a good place to start.

- If you cannot calculate the XLD exactly, here is a good approximation [Table 2]: Simply multiply the functionality of each polyol by its percent in the polyol blend, and then total these partial functionalities to obtain the average total functionality of the polyol blend. For example: see Table 2.

<table>
<thead>
<tr>
<th>Table 2: Calculation of Polyol Average Functionality</th>
</tr>
</thead>
<tbody>
<tr>
<td>POLYOLS</td>
</tr>
<tr>
<td>PS2352</td>
</tr>
<tr>
<td>R315x</td>
</tr>
<tr>
<td>Voranol 360</td>
</tr>
<tr>
<td><strong>Total</strong></td>
</tr>
</tbody>
</table>

An average functionality greater than three is highly desired. If the result is less than 3 [Table 2a], you will have difficulty using ecomate successfully, especially in lower density foams, because of shrinkage. If the desired system contains a high level of plasticizers [such as fire retardants, viscosity reducers, etc], then a higher average functionality may be required.

The exact functionality value one needs always depends on the environmental conditions that the foam will see under actual use conditions, the more stringent they be - the greater the need. And while one is reformulating,
bear in mind to use enough of those polyols which afford good ecomate retention to garner combustible rated formulations [Figure 1].

These curves are from single members of each type polyol. As there are wide variations amongst the members of each polyol class as a result of differences in polyol viscosity, PO/EO quantity and ratio, and polyol co-blends [such as sucrose/glycerin], flash point testing of specific individual blends is always warranted!

![Polyol Type Graph]

**Figure 1: Effect of Polyol TYPE on Flash Point of Ecomate / Polyol Mixtures**

- **ADJUSTMENT OF THE SURFACTANT:** Why adjust the surfactant? Because the surfactant has a great influence upon the success of any formulation – it affects the density of the foam, the cell structure of the foam, and most importantly the thermal properties of the foam. And in a lesser way, the surfactant can influence the can or shelf stability and the flammability of the foam formulation. The surfactant can influence properties not only by its type [its backbone chemistry and end capping], but also from the quantity used.

- When we first developed ecomate blown systems, a study of surfactant types was conducted by FSI at a major surfactant supplier. In that study we investigated in the same system a broad spectrum of surfactants – ranging from rigid to flexible - to discern differences in cell characteristics and flow. Ecomate was so forgiving that no failures occurred with any surfactant, and the flow characteristics seemed identical. There were only minor differences in cell size. While we initially found this encouraging, we now know it was only the tip of the iceberg – the surfactant choice can be critical for success.

A recent surfactant study compared five surfactants run at the same load level in the same formulation. A 2500 gram master batch of the formulation was made without any surfactant; the resulting batch then was split into 5-400g sub-batches and the respective surfactant was added at a rate of 4g/400g of mix. Hand-mixed foams were then made with each formulation. The density results are shown in Figure 2:
RESULTS of STUDY

- Surfactant 3 & 4 gave lower density foams than the first surfactant, while surfactant 5 is higher.
- Nearly the same trend followed with the 6 day Humid Aging samples [Figure 3]
  - Surfactants 3 & 4 having greater volume change.
- The compressive strengths [normalized for 2 pcf density] show essentially the same trend [Figure 4]
- Because this was the IDENTICAL SYSTEM except for surfactant, this strongly suggests that surfactant choice affects:
  - Density,
  - Compressive strength, and
  - Humid aging.

Figure 2: Effects of Surfactant type on foam density

Figure 3: Effect of Surfactant on Dimensional Stability after 6 days at 158°F / 100% RH
While the values obtained for the wet [158°F/100% RH] dimensional stability [Figure 3] seem like very high numbers, bear in mind that they were obtained on free rise foams at ~ 2.0 pcf without any packing.

So, what is unique about the foams made with surfactants 3 & 4? They tended to have the finest cell structures of all the foams produced, with surfactant 4 having the finest. Surfactant 4 also had the best [lowest] thermal conductivity numbers of the group. Intuitively this makes sense: finer cell structure results from greater compatibility of the reactants which leads to lower density foams and to better k-factors. Why? Because more of the blowing agent is captured in the cells, and there are more cells for heat to traverse, hence a lower k-factor. If the cell structure becomes too fine, however, the cell struts become weaker – hence lower compressive strengths, and a greater tendency to shrink! Both these effects are part of the nature of ecomate blown foams – they have naturally finer cell structures because of the improvement in compatibility ecomate affords. This suggests that less surfactant might be used.

All surfactant are not created equal, as can be seen by the data already presented. We have seen that the surfactant choice can affect density, strength, dimensional and thermal properties. They can also affect the amount of water absorption of a foam formulation [Figure 5].

CAN STABILITY

System [shelf or can] stability is another area in which proper surfactant choice can benefit a foam formulation. We noticed early on in our development work with ecomate that the density of certain ecomate systems were drifting [the densities were climbing] over a period of time, yet there was no change in reactivity. At the same time the cell structure of the foam was becoming more open and coarse, and the thermal conductivity was becoming poorer. While natural for all foams to exhibit thermal drift [the subject of an earlier paper¹], thermal drift in the can means a change in the formula chemistry – especially with the surfactant

Suspecting the surfactant, a set of experiments were run to examine the stability of several surfactants in the same polyol mixture when aged at 120°F [49°C] for over a month [Figure 6]. The principle changes seen in this aging were in cell fineness and in thermal conductivity [both worsened].

The thermal insulation values obtained [Figure 6] at RT were from hand mixed foams and are relative to one another, and are not comparable [are higher] to those obtained by machine mixes. This data indicates that the choice of a proper surfactant is very important to obtaining good thermal properties, and they also play a major role in maintaining long term shelf [and thermal] stability.
Figure 5: Weight gain in Humid Aging caused by surfactant type choice

FOAM FLAMMABILITY

A study of surfactant effects upon foam burning was conducted after it was discovered that the type and amount of surfactant weighed heavily upon burning characteristics. In developing a Class 2 pour, different surfactants were added at 1 weight % of the identical polyl component. Results from a modified 2 foot Monsanto Mini Tunnel are shown in Table 3 which shows the effect on Flame Spread and Smoke [relative numbers]. Surfactant 2 had superior results, while surfactant 4 degraded the burn properties.

When surfactant was added to the Isocyanate component [in addition to that in the polyl side] of a low Index Class 1 spray, the incremental additions became increasingly more flammable [Table 4], demonstrating that type and quantity of surfactant are both important.

LAMINATE BOARDSTOCK RUNS

To demonstrate the extent of good results that can be obtained using ecomate in a nearly optimized laminate board, we include the following line run data from two laminate producers, one a drop-in, the second further modified by changing slightly the polyl blend and the surfactant type and level [lessened].

The first Lamination system [Trial 1 - Table 5] was “optimized” only to the extent that adjustment was made to obtain equal reactivity and uniform density. The ecomate system required 4% less catalyst! The rest of the system remained intact. It was essentially a drop-in evaluation!

As a result, the ecomate system was 14% weaker parallel to rise, and 15% weaker perpendicular to rise. It was slightly poorer in dimensional stability, albeit slightly better in thermal conductivity [0.5 mW/m.K]. Flammability was improved in both the M45 and B-2 tests. This system was formulated for pentane, and because of a reluctance to reformulate, the customer saw little benefit.
Figure 6: Thermal drift with certain surfactants aged in system for 35 days at 120°F [Hand mixed]

Table 3: Effect of surfactant type on Flame Spread and Smoke at 1% loading in identical Class 2 Pour

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>FS</th>
<th>Smoke</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surf 1</td>
<td>25</td>
<td>40.7</td>
</tr>
<tr>
<td>Surf 2</td>
<td>20</td>
<td>28.8</td>
</tr>
<tr>
<td>Surf 3</td>
<td>35</td>
<td>39.6</td>
</tr>
<tr>
<td>Surf 4</td>
<td>50</td>
<td>&gt;70</td>
</tr>
<tr>
<td>Surf 5</td>
<td>25</td>
<td>28.8</td>
</tr>
</tbody>
</table>

Table 4: Effect of A-side Surfactant Levels on Burn Resistance

<table>
<thead>
<tr>
<th>% Surfactant</th>
<th>FS</th>
<th>Smoke</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>23</td>
<td>8.5</td>
</tr>
<tr>
<td>0.1</td>
<td>23</td>
<td>10.9</td>
</tr>
<tr>
<td>0.3</td>
<td>25</td>
<td>16.4</td>
</tr>
<tr>
<td>0.65</td>
<td>30</td>
<td>31.9</td>
</tr>
</tbody>
</table>

The second lamination system's data [Trial 2 - Table 6 & Figure 7] shows the impact of optimization for thermal conductivity. The control is a commercialized pentane blown laminate boardstock system run on a line producing foil-faced board, at that moment 4 inch thick. The ecomate system optimization was for lowest thermal values. The ecomate system was run under the same conditions on the same line with the same catalyst blend, the transition between systems done on the fly. This system, in addition to the markedly improved [15% better] initial and long term thermal properties mentioned above, shows equivalent physicals and improved flammability [lower FS and smoke values in a small scale E84 tunnel test] over the control.
Both laminate system trials, Trial 1 and Trial 2, [Table 5 and Table 6] were blown with the identical blowing agents — differences in physical properties are due to the different polyols and surfactants used between each trial — thus dramatically demonstrating the benefits of optimization.

Table 5: Non-Optimized Ecomate Boardstock Run Physicals

<table>
<thead>
<tr>
<th>PROPERTY</th>
<th>PENTANE</th>
<th>ECOMATE</th>
<th>units</th>
</tr>
</thead>
<tbody>
<tr>
<td>CREAM</td>
<td>15</td>
<td>15</td>
<td>s</td>
</tr>
<tr>
<td>FIRM</td>
<td>40</td>
<td>39</td>
<td>s</td>
</tr>
<tr>
<td>DENS</td>
<td>25.4</td>
<td>25.4</td>
<td>kg/m3</td>
</tr>
<tr>
<td>CS/</td>
<td>189</td>
<td>162</td>
<td>kPa</td>
</tr>
<tr>
<td>CS_1_</td>
<td>85</td>
<td>72</td>
<td>kPa</td>
</tr>
<tr>
<td>DS+5</td>
<td>-0.22</td>
<td>-0.3</td>
<td>%</td>
</tr>
<tr>
<td>DS-15</td>
<td>-0.27</td>
<td>-0.32</td>
<td>%</td>
</tr>
<tr>
<td>Lambda,10°C</td>
<td>22.04</td>
<td>21.49</td>
<td>mW/m.K.</td>
</tr>
<tr>
<td>B2</td>
<td>14.2</td>
<td>13.6</td>
<td>cm</td>
</tr>
<tr>
<td>M45</td>
<td>4.9</td>
<td>4.5</td>
<td>%</td>
</tr>
</tbody>
</table>

The extent of optimization in Trial 2 was a mere change in polyol and surfactant — yet it made a marked change in the physical properties! This is what we would ask you to do to make ecomate work for you.

Not only does the ecomate blown system here in Trial 2 give a lower initial lambda [k-factor], but it exhibits less thermal aging over 210 days than the commercial Pentane system [Figure 7]. Testing continues on these systems.

The purpose of this paper was not to be a treatise on the choice of proper surfactants — but to show that by proper reformulation and optimization, excellent results can be obtained with ecomate blown foam systems. We hope you will be receptive to what we have shown you!
### TABLE 6: Optimized for Lambda - Commercial Boardstock and Ecomate Systems

<table>
<thead>
<tr>
<th>TRIAL 2</th>
<th>CONTROL</th>
<th>ECOMATE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dens, pcf</td>
<td>1.75</td>
<td>1.97</td>
</tr>
<tr>
<td>CCC, %</td>
<td>98.5</td>
<td>94.6</td>
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</table>

<table>
<thead>
<tr>
<th>Δ%Vol, 7days</th>
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</thead>
<tbody>
<tr>
<td>COLD</td>
</tr>
<tr>
<td>WET</td>
</tr>
<tr>
<td>DRY</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CS //, psi</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>K-factor, 20°F</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1377</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Lambda, -6.7°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>19.8</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>FS*</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Smoke</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
</tr>
</tbody>
</table>

- The FS and Smoke values were obtained in small scale testing and are not meant to indicate what might occur in a real fire scenario.

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**Figure 7:** The benefit of optimized ecomate system over control [a commercialized 70:30 cC₅:iC₅ Blown System]
SUMMARY

1. Most formulators initiate any evaluation in a “drop-in” mode.
2. Ecomate systems naturally have finer cell structures than other systems
   a. It is more compatibilizing than other BAs.
   b. It is a stronger solvent than other BAs
3. The combination of stronger solvency and finer cells can lead to shrinkage
4. Optimization is recommended for success!
   a. Increasing the XLD of the polyl blend
   b. Changing the surfactant type and amount
      i. Not all surfactants are created equal
5. All foam system can benefit from optimization.
   a. To get the most out of the formulation one brings to market
   b. Without increasing costs, and
   c. Potentially ending up with vastly superior properties
6. Ecomate has all the properties you might want
   a. Excellent thermal properties
   b. Excellent environmental properties
   c. Low molar cost
   d. Excellent miscibility with all raw materials
   e. The ability to produce systems w/o flammability issues
7. It can work for you - if you are willing to reformulate
8. This can be the LAST reformulation you may have to make!
9. We are here to work with you and help you on a one-to-one basis.

DEDICATION: This paper is dedicated to the memory of our good friend and colleague, Dr John F. Timberlake, who [among many other things] spent many moments making suggestions for and redacting these papers. He died suddenly in his sleep on March 9th, 2011. He will be missed by all of us.
John A. Murphy

John received his BS in Chemistry in 1965. During his 35 years researching urethanes he has worked for [among others] ARCO Chemical and Elf Atochem, where he introduced HCFC-141b to the industry. Currently employed by FSI, he is responsible for New Product Development - Ecomate.

David L. Modray

David received his BS in Chemical Engineering in 1995 from the University of Missouri-Columbia. For 15 years he has been employed by FSI as a research chemist. He has been formulating with ecomate for the last 12 years.

3J. Murphy, “Long Term Aging of Closed-Celled Foam Insulation”, CPI Annual Polyurethane Technical/Marketing Conference 2010, Houston TX, Session Construction2, paper 21
The Benefits of Optimization In Ecomate® Blown Foams

CPI 2011 - Nashville, TN
AGENDA

• Déjà vu! The Ghost of BAs Past
• Advantages [& Disadvantages] of Ecomate
• Why Optimize !
• 2 Steps for success
  ‣ Increase Polyol Average Fn
  ‣ Surfactant Adjustment
• Why adjust Surfactant? Its Effects
• The Benefits of Optimization - Commercial Trials
• Summary
Abstract

“The mandated switch has **required producers to make numerous formulation changes** due to the differing physical properties.

- higher boiling point, higher latent heat of vaporization,
- **increased polymer solubility**, and
- decreased viscosity of the polyol and isocyanate blends.

**increased solubility** has led to

- **a reduction in compressive strength**, and
- **problems with dimensional stability**.

improving foam processing and dimensional stability

- with **the use of high functional, low equivalent weight polyols** and
- **increased viscosity and higher functionality Polymeric MDI (PMDI)”**
Suitability of ecomate

- Well suited BA for PUR & PIR foams
- Similar to HCFC-141b
  - BP identical: [32°C]
  - LFL slightly lower: [5 vol% vs. 7.6 vol%]
  - When blended into polyols – Flammability a non-issue!
  - Solubility stronger with ecomate
- Not a Drop-In for all systems
  - Requires Optimization [like any other BA]

<table>
<thead>
<tr>
<th>Table 1</th>
<th>ecomate</th>
<th>141b</th>
</tr>
</thead>
<tbody>
<tr>
<td>MW</td>
<td>60</td>
<td>117</td>
</tr>
<tr>
<td>BP, °C</td>
<td>32</td>
<td>32.2</td>
</tr>
<tr>
<td>Flash Pt, °C</td>
<td>-32</td>
<td>-</td>
</tr>
<tr>
<td>LFL, ppm</td>
<td>50000</td>
<td>76000</td>
</tr>
<tr>
<td>Lambda</td>
<td>10.7</td>
<td>10</td>
</tr>
<tr>
<td>ODP</td>
<td>0</td>
<td>0.11</td>
</tr>
<tr>
<td>GWP</td>
<td>~1</td>
<td>725</td>
</tr>
<tr>
<td>VOC</td>
<td>exempt</td>
<td>exempt</td>
</tr>
</tbody>
</table>
Advantages of ecomate

- **Low Gas Lambda**
  10.7 mW/m.K

- **Environmentally Benign**
  - Zero ODP,
  - minimal GWP,
  - VOC-exempt

- **Very Cost Efficient**
  - Lowest MW  60 g/mol
  - Low Cost
  - Pricing independent of Petrochemicals

- **Your LAST Transition!**

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</tr>
</tbody>
</table>
Ecomate Hurdles

1. It can **HYDROLIZE**!
   - An ESTER

2. Slightly More **FLAMMABLE** than 141b
   - Only in Neat form \( LFL = 50,000 \text{ ppm} \)
   - In Polyols – can handle conventionally like 141b

3. Slightly Stronger **SOLVENCY**
   - Can lead to Shrinkage!
Hurdle 1 - HYDROLYSIS

- Techniques available for STABILIZING
  - Up to ONE YEAR
    - Inhibit Hydrolysis
    - Protect Catalyst package
  - Shared with Customers with NDA signing
Hurdle 2 - FLAMMABILITY

- Minimal plant modifications
  - Far fewer than with HC conversion
- Once blended into polyol
  - Are classed NON-FLAMMABLE
  - Can beHandled / Shipped w/o RED PLACARDS
- We can advise you!
Hurdle 3 – SHRINKAGE

- Fix depends on the TRANSITION
  - From HCFC -141b - Easy
  - From HFCs - More involved
  - From HCs - Mind Set Change

- Each Requires OPTIMIZATION!

- May require Minimal REFORMULATION
Optimization - Necessary for any transition!

• From 141b –
  ▸ Mandated change
  ▸ Stronger solvency w Ecomate
  ▸ Potential Fixes
    - Increase Index ~ 10 points
    - Add more water; use less ecomate
      ◦ Both easy, but more expensive
    - Reformulate
      ◦ SLIGHT changes
Optimization - Necessary for any transition!

• From HFCs –
  ‣ Driven by VARIOUS PRESSURES
    - Environmental
    - Economic
  ‣ Desire for LAST Transition
  ‣ Slight Reformulation –
    - because of stronger solvency
Optimization - Necessary for any transition!

• From **HCs** –
  ‣ **HC Solubility** is much POORER than ecomate
  ‣ **Already Reformulated to use HCs:**
    - Converted to PA ester,
    - more FRA,
    - lower visc polyols
    - Higher amounts of surfactant
  ‣ **Reformulation again necessary!**
Reformulation ADVANTAGES

• Converting from HCs to Ecomate
  ‣ IS ASTUTE:
    - Less FRA [~20% less] needed
    - Lower surfactant levels
    - Lower catalyst levels
    - Lower BA levels
  ‣ Improved Thermal Props
Optimization Steps

• Two Minor Steps
  ‣ Step 1: Shorten the XLD of the polymer
  ‣ Step 2: Change Surfactant
    - Type & Amount (lessened)
**Step 1: Adjusting the XLD**

- Decrease the Avg XLD
- Or
- Increase the Avg Fn

**Target:** Fn >3

---

### Table 1a

<table>
<thead>
<tr>
<th>POLYOLS</th>
<th>OH#</th>
<th>fn</th>
<th>EqWt</th>
<th>Mn</th>
<th>AMT</th>
<th>avg fn</th>
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<tr>
<td>PS2352</td>
<td>240</td>
<td>2</td>
<td>233.8</td>
<td>467.5</td>
<td>50%</td>
<td></td>
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<tr>
<td>R315x</td>
<td>315</td>
<td>3.2</td>
<td>178.1</td>
<td>569.9</td>
<td>50%</td>
<td></td>
</tr>
<tr>
<td>Voranol</td>
<td>360</td>
<td>4.5</td>
<td>155.8</td>
<td>728</td>
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<td>2.54</td>
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</table>

### Table 1b

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<th>OH#</th>
<th>fn</th>
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<th>AMT</th>
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<td>728</td>
<td>25%</td>
<td>3.09</td>
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</table>
Step 2: Surfactant Change

• Why change the surfactant?
  ‣ It Affects:
    - Foam DENSITY
    - CELL STRUCTURE
    - THERMAL PROPERTIES
  ‣ It may Affect
    - Shelf Stability
    - Flammability
  ‣ Let’s take a look....
Surfactant Study Run:

• Same HANDMIX Formulation
  ‣ Master batch w/o Surfactant
    - Split into 5 Batches
  ‣ Five different Surfactants
    - Added at 1 part /100 parts formula
  ‣ Studied the Effects
Density Effects

Surfactant on Density

Density, pcf

Surfactant
Compressive Effects

Normalized Compressives

Strength at 2 pcf, psi

Surfactant

1 2 3 4 5

CS//
CS_|_
Humid Age Effects

6d WET DS

% Original VOL

Surfactant

- Avg Change

Better Products. Better for the Environment
Surfactants – on FLAMMABILITY

Class II Pour - 1% Surfactant loading

Surfactant

Flame Spread

1 2 3 4 5

0 10 20 30 40 50 60

Better Products. Better for the Environment
STUDY RESULTS

• Same Pattern
  ‣ Surfactant 3 & 4 poorer properties than rest
  ‣ They also had FINEST CELLS
    - Finer Cells = better thermals
    - Finer Cells = poorer physicals
• Ecomate produces foams with
  ‣ Naturally finer cells
    - Due to Improved Compatibility
    - Less Surfactant needed
Surfactant Aging

SURF AGING – HAND MIXED

DAYS Shelf Aged at 120°F

- SURF A
- SURF B
- SURF C
- SURF D
Surfactant CHOICE affects:

- MOST MAJOR PROPERTIES
  - DENSITY
  - STRENGTH
  - SHRINKAGE
  - THERMAL PROPS
  - SHELF STABILITY
The Benefits of Optimization – Line Trials

- TWO Full Production Laminate Trials
  - TRIAL 1 – RXN & DENS adjustment only
  - TRIAL 2 – Optimized for Thermals only
- BOTH used the IDENTICAL BAs
  - Differences due to Polyols & Surfactants
  - Show Benefits of OPTIMIZATION
Laminate Optimization 1

• System 1
  ‣ Pentane blown \([70:30 \text{ cC}_5:\text{iC}_5]\) vs Ecomate
  ‣ Drop-In Substitution
  ‣ Minimal Optimization
    - Uniform Density
    - Equal Reactivity
  ‣ USED 4 % LESS CATALYST w ECOMATE
NON-OPTIMIZED LAMINATE RUN #1

- RXN Rate & DENSITY same
- STRENGTH poorer w Ecomate
- STABILITY ~ Same
- LAMBDAA IMPROVED!
- BURNS IMPROVED!

<table>
<thead>
<tr>
<th>PROPERTY</th>
<th>PENTANE</th>
<th>ECOMATE</th>
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<tbody>
<tr>
<td>CREAM</td>
<td>15</td>
<td>15</td>
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<tr>
<td>FIRM</td>
<td>40</td>
<td>39</td>
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<tr>
<td>DENS</td>
<td>25.4</td>
<td>25.4</td>
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<tr>
<td>CS//</td>
<td>189</td>
<td>162</td>
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<tr>
<td>CS_</td>
<td>_</td>
<td>85</td>
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<tr>
<td>DS+5</td>
<td>-0.22</td>
<td>-0.3</td>
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<tr>
<td>DS-15</td>
<td>-0.27</td>
<td>-0.32</td>
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<tr>
<td>Lambda</td>
<td>22.04</td>
<td>21.49</td>
</tr>
<tr>
<td>B2</td>
<td>14.2</td>
<td>13.6</td>
</tr>
<tr>
<td>M45</td>
<td>4.9</td>
<td>4.5</td>
</tr>
</tbody>
</table>
Laminate Optimization 2

- **System 2**
  - Pentane blown \([70:30 \text{ cC}_5: \text{iC}_5]\) v Ecomate
  - 4” THICK
    - Foil faced
  - Optimized for Thermal Properties
OPTIMIZED LAMINATE RUN #2

- DENSITY higher,
  - RXN Rate SAME

- STABILITY similar

- CS // poorer

- FLAMMABILITY IMPROVED

- THERMALS VASTLY IMPROVED [10-15%]

<table>
<thead>
<tr>
<th></th>
<th>Trial 2</th>
<th>C5 CONTROL</th>
<th>ECOMATE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density, pcf</td>
<td>1.75</td>
<td>1.97</td>
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<tr>
<td>CCC, %</td>
<td>98.5</td>
<td>94.6</td>
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</tr>
<tr>
<td>Δ%Vol, 7d</td>
<td></td>
<td></td>
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<tr>
<td>COLD</td>
<td>0.98</td>
<td>-0.7</td>
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<tr>
<td>WET</td>
<td>4.11</td>
<td>5.06</td>
<td></td>
</tr>
<tr>
<td>DRY</td>
<td>3.03</td>
<td>4.35</td>
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<tr>
<td>CS //, psi</td>
<td>20.3</td>
<td>12.9</td>
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<tr>
<td>FS*</td>
<td>30</td>
<td>25</td>
<td></td>
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<tr>
<td>Smoke</td>
<td>400</td>
<td>180</td>
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<tr>
<td>K-factor, 20°F</td>
<td>0.134</td>
<td>0.118</td>
<td></td>
</tr>
<tr>
<td>Lambda, -6.7°C</td>
<td>19.8</td>
<td>16.9</td>
<td></td>
</tr>
</tbody>
</table>
OPTIMIZED LAMINATE RUN #2 – AGED 210 DAYS

ECOMATE = BETTER k-FACTORS, LESS THERMAL DRIFT
CONCLUSIONS

• OPTIMIZATION – Always Required!
• Surfactant choice affects:
  ‣ DENSITY
  ‣ STRENGTH
  ‣ SHRINKAGE
  ‣ THERMAL PROPS
  ‣ FLAMMABILITY
• FOAM FUNCTIONALITY – Critical with ECOMATE
Summary:

- Ecomate systems naturally have fine cell structures
  - more compatibilizing than other BAs.
  - a stronger solvent than other BAs
- Stronger solvency and finer cells could lead to shrinkage
- Optimization is recommended for success!
  - Increasing the Fn of the polyol blend
  - Changing the surfactant type and amount
    - Not all surfactants are created equal
With OPTIMIZATION

• Ecomate has all the properties you might want
  ‣ Excellent THERMAL PROPERTIES
    - Better thermal aging than HCs
  ‣ Excellent PHYSICAL PROPERTIES
  ‣ AS WELL AS:
    - Excellent environmental properties
    - Low molar cost
    - Excellent miscibility with all raw materials
    - The ability to produce systems w/o flammability issues

• All foam systems can benefit from optimization.
  ‣ Get the most out of YOUR Formulation
    - Without increasing costs, and
    - With the potential of vastly superior properties
Thank you for your time.

www.foamsupplies.com

www.ecomatesystems.com