

Factors contributing to k-factor optimization with ecomate® blown foams

JOHN MURPHY

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

ABSTRACT

Many factors influence the thermal efficiency [or k-factor] one obtains with foams blown with any of the commercial physical blowing agents. Factors affecting a products thermal efficiency depend on, but are not limited to, the blowing agent itself – such as the blowing agent's molecular weight, its boiling point, or its solubility in the foam matrix. Other factors depend on formulation parameters such as catalyst levels which affect speed of reaction and fineness of cell structure. Yet others depend on the mixing efficiency of the equipment used to process the foams. Finally, a great deal of the contribution depends on the amount of protection the foam receives from its immediate environment - ranging from exposed foam to foam enclosed within impermeable facers.

In this paper, designed experiments will explore the effects of formulation parameters, such as catalyst or surfactant type and amount, polyol and isocyanate type, and of course blowing agent blend have on thermal efficiency. We will also show the effects of mixing efficiency, foam flow and density have on this important criterion. Based on these results we will show how to optimize formulations to best utilize ecomate for blowing rigid urethane foams.

BACKGROUND

Fewer and fewer blowing agents are suitable for blowing rigid polyurethane foams. Of these few blowing agents, each has its unique benefits; each has its weak points. More of those blowing agents currently used will disappear due to environmental regulation in the near future. Those that remain will have increasing demands put on them to perform to the criteria previously expected of their predecessors, because the industry has gotten to where it is by utilizing those available raw materials to their limits.

For example, the industry cut its eye teeth on trichlorofluoromethane, or CFC-11, which was a non-flammable liquid at room temperature. More importantly, it had a huge molecular weight [MW = 137] due to its fluorine and chlorine content, which allowed foams made from it to have excellent thermal properties. Why? Because it takes a lot more energy [heat] to move a large molecule than it does a smaller one. But size [molecular weight] is not the main thing influencing thermal efficiency, as we shall shortly see.

Bearing these principles in mind, each succeeding generation of blowing agents has had its challenges, but we have learned to use them, and use them well. In fact, it might be said that transitions, painful as they were, allowed the industry further insight into the mechanisms of good insulation, and we have learned a great deal along the way. For example, with the introduction of HCFC-141b [which was a much stronger solvent than R-11] we learned that the use of a little water in the formulation [required to cut the solvency of 141b] made a much finer cell structure in the foam and actually improved its thermal properties. So it is the goal of this paper to present to the reader some of the factors that can be used to improve the thermal efficiency of foams blown with ecomate.

EXPERIMENTAL

Hand mix foams were usually made with 100 to 300 gram mixes at 2000 rpm in a 1 liter beaker. Hand mixes were poured into a 9" x 9" open box. Machine mixed foams were run on SLUG low pressure equipment at 15 to 45 lbs/min output, or on a Gusmer RimCell C series High Pressure unit at 80 to 100 lbs/min output. Machine mixes were molded in a 2000mm x 200mm x 50mm Lanzen Mold maintained at 110 °F.

Thermal conductivities were measured on a LaserComp Fox 200 heat flow meter, which takes samples 8"x8"x 2" maximum. Results in this paper are given in mW/m²K for lambda, and in BTU*in/hr*ft²*°F for k-factors. Results were at 75 ± 25 °F unless otherwise indicated.

Experiments were designed and analyzed with Design-Expert® software, version 6.0.1 by Stat-Ease.

PROPERTIES

The physical properties of ecomate have been compared to those of other BAs in previous papers^{1,2,3}. We will briefly revisit them in **Table 1**.

Table 1	<u>ecomate</u>	<u>141b</u>	<u>HFC</u> <u>245fa</u>	<u>HFC</u> <u>365mfc</u>	<u>n-</u> <u>pentane</u>	<u>Cyclo-</u> <u>pentane</u>
Molecular Wt	60	117	134	148	72	70
Boiling Point, °C	31,5	32	15,3	40,2	36	49
Sp Gr.	0,982	1,24	1,32	1,25	0,62	0,75
Lambda, gas @ 25°C	10,7	10	12,2	10,6	14*	11*
LEL/UEL, %	5 - 23	7,6-17,7	n/a	3,5-9	1,4-17,8	1,4-8,0

* 20 C

Because ecomate is a smaller molecule than most others, it requires less quantity than the others to blow foams of equal density, a decided cost advantage. Because ecomate is a stronger solvent than most, it is capable of incorporating all the types of raw materials formerly utilized with 141b. This gives the formulator more latitude in his box of tricks. But because of its higher solvency, some additional water might be used to improve stability. Therein lies the rub: How to get the maximum thermal conductivity from ecomate blown foams when it seems that some water is required.

First of all, where does ecomate stand in the realm of things? For **Table 2** we prepared a common lot of polyol component and added ecomate, 141b, and 245fa on a molar basis to obtain common density foams with each BA; and poured hand-mix boxes of foam. Two inch thick samples were then tested at a mean temperature of 75 °F. As can be seen, the ecomate and the 245fa blown foams were nearly the same, while the 141b foam was markedly better. This belies the traditional philosophy that higher MW always gives lower lambda values. Bear in mind that the values obtained here are high because these are hand-mix samples.

Table 2	Blowing Agent	k-factor	mW/m ² K
J066-2	141b	0.188	26.99
J066-3	245fa	0.201	28.87
J066-1	ecomate	0.204	29.42

The thermal efficiency of foam can be affected by the mean temperature at which it is tested. In general, the lower the test temperature, the lower [better] is the thermal conductivity [Figure 1].

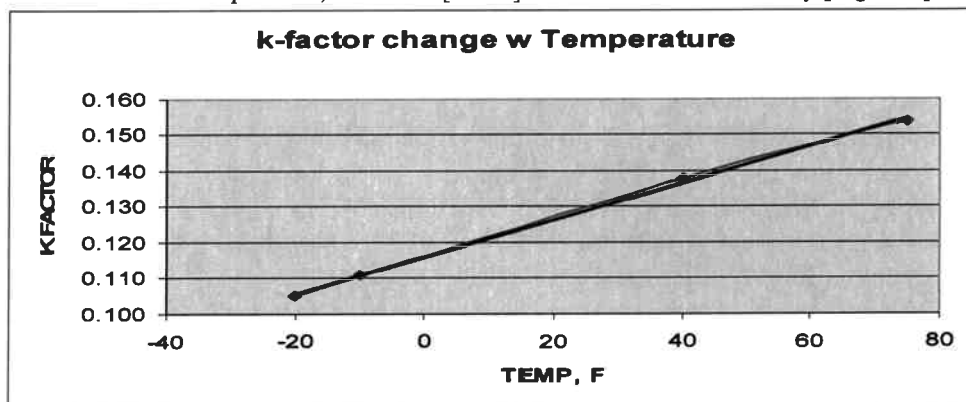


Figure 1: Temperature / Thermal Conductivity Dependence

The thermal efficiency of foam can be manipulated by changes in formulation and in changes in processing. For example:

PROCESSING EFFECTS

Mixing

A designed experiment [using Design Expert 6.0.1 from Stat-Ease] was set up to examine the hand mix effects of mixer speed, mix time, pour size and surfactant amount on thermal conductivity. Mix speed was varied from a low value of 1000 rpm to a high value of 3000 rpm; mix time from 5 to 10 seconds, pour size from 150 to 300 grams total mix; and surfactant concentration from a low concentration of 1% to a high concentration of 2 wt% of the entire mix. The entire set of experiments [20 runs] was run as two blocks as shown in Table 3.

Table 3: Mixing Effects Factorial							
RUN	BLOCK	MIX SPEED, rpm	POUR SIZE, gm	SURF CONC, pct	MIX TIME, sec	k-FACTOR, BTU.in/hr.ft ² .F	LAMBDA mW/m ² K
3	1	1000	150	1	10	0.206	29.68
14	2	1000	150	1	5	0.207	29.73
10	1	1000	150	2	5	0.210	30.24
12	2	1000	150	2	10	0.203	29.15
1	1	1000	300	1	5	0.210	30.18
11	2	1000	300	1	10	0.203	29.14
6	1	1000	300	2	10	0.206	29.62
18	2	1000	300	2	5	0.199	28.59
4	1	2000	225	1.5	7.5	0.203	29.28
9	1	2000	225	1.5	7.5	0.200	28.80
17	2	2000	225	1.5	7.5	0.202	29.06
19	2	2000	225	1.5	7.5	0.199	28.67
8	1	3000	150	1	5	0.206	29.65
20	2	3000	150	1	10	0.204	29.36
5	1	3000	150	2	10	0.205	29.48
15	2	3000	150	2	5	0.199	28.57
2	1	3000	300	1	10	0.201	28.99
16	2	3000	300	1	5	0.203	29.14
7	1	3000	300	2	5	0.196	28.14
13	2	3000	300	2	10	0.195	28.02

The statistically significant results indicate that:

- A faster mix speed result in lower lambda values [figure 2];
- A larger pour result in lower lambda values [figure 3]; and
- A higher surfactant concentration gave lower lambda values [figure 4].
- The duration of the mix was not statistically significant.

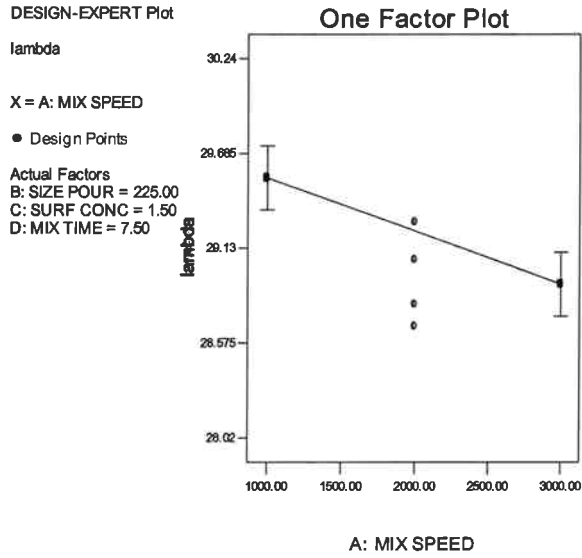


Figure 2: MIX SPEED on Lambda

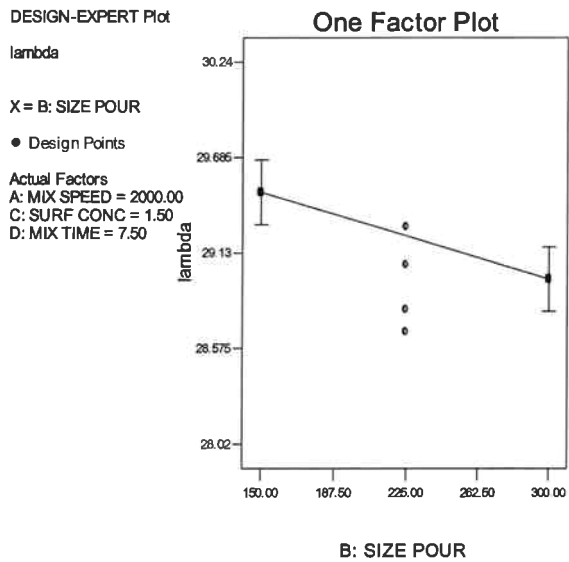


Figure 3: POUR SIZE on Lambda

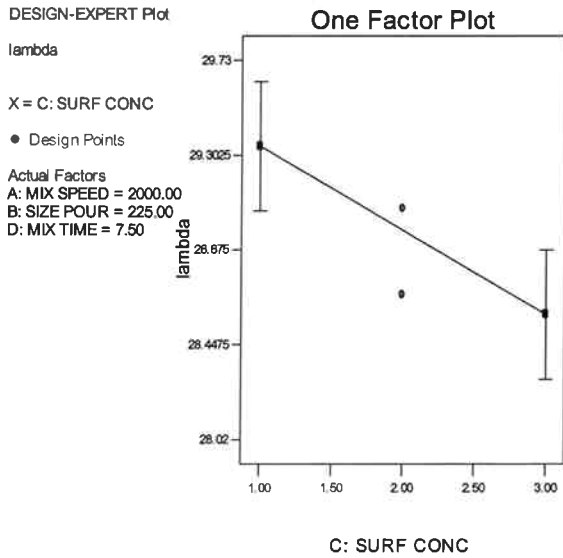


Figure 4: SURF CONC on Lambda

Hence, there ARE indeed processing parameters that can significantly affect getting the low lambda values we all seek. Faster mix speed will give better more intimate mix, resulting in finer cells, contributing to lower lambda. A larger pour results in a lower surface area per volume of mix, hence lower BA loss; higher surfactant content also lessens BA loss.

In fact, there is a statistically significant interaction between **high mix speed and high surfactant amount resulting in lower density foam [Figure 5]**. In fact, this figure clearly shows that the benefit of a higher loading of surfactant can be lost if the mix speed is low!

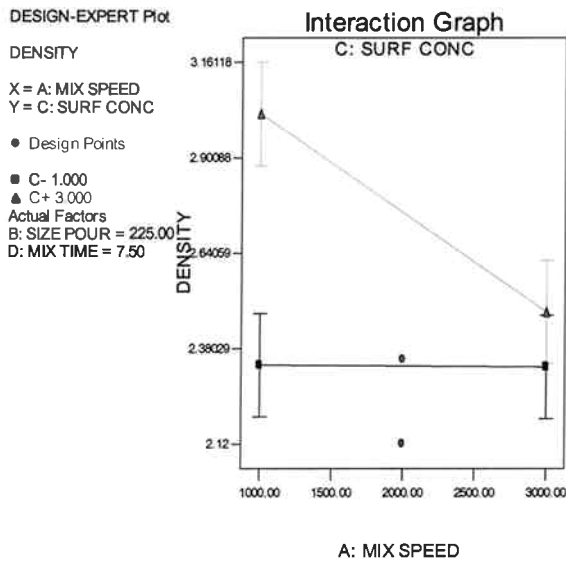


Figure 5: SURF CONC / MIX SPEED on DENSITY

Lower density foams generally have lower thermal conductivity because they have a higher quantity of foam blowing agent per mass of foam.

Hand mix v Machine

Machine mixed foams always give lower [better] thermal properties than hand mixes [Table 4]. The data also demonstrates that the degree of over packing can negatively influence thermal conductivity.

Table 4: Machine v Handmix, Over Pack Effects

K-FACTOR	91-5	91-6	91-8
HANDMIX	0.191	0.192	0.200
MACHINE	0.156	0.158	0.160
LAMBDA	91-5	91-6	91-8
HANDMIX	27.5	27.6	28.7
MACHINE	22.5	22.7	23.0
OVER PACK	91-5		
7%	0.158		
12%	0.160		
19%	0.164		

Direction of Rise

Just as orientation of a mold [vertical v horizontal] can affect the orientation of the cells and affect the compressive strength of the foam, it can equally affect the thermal properties of the foam. It is well known that foam is stronger in the long axis. Consider a foam that has an aspect ratio of 2 [i.e., its cells are 2 times longer than wide]. It will have twice as many cells per unit measure in the narrow direction [perpendicular to rise] as in the long direction [parallel to rise]. So heat will have a shorter path to travel [fewer cells to traverse] in the parallel to rise direction, and thermal properties will be worse in this direction. Surfactant choice can help in two ways, by making finer cells and affecting the spherical nature of the foam. But surfactant cannot easily overcome direction of rise!

FORMULATION EFFECTS

Ecomate, because of its excellent solubility, can be substituted into a formulation on a stoichiometric basis in lieu of any other foam blowing agent. Nevertheless, one may want to reformulate to get the best properties from this unique raw material. The trade-off is optimal properties versus the cost of reformulation. The purpose of this section is to give some insights into those changes that will allow faster optimization, with selection of the most efficacious raw materials.

Surfactant Effects:

As previously mentioned, the quantity of surfactant can have a marked influence on the thermal efficiency of the foam. This seems obvious if one thinks of the many roles the surfactant plays in the foam: it compatibilizes the ISO with the Polyol; it forms the cells; determines the relationship between strut and window thickness; and it determines if the cell windows remain closed, to name a few.

Not only does surfactant *quantity* play a role, but also its *type* as well. This has thoroughly discussed in a paper written by Degussa⁴. In particular, the molecular weight, siloxane content, and degree of modification have strong bearing on the fate of the foam produced, especially its density and thermal conductivity. We have found marked differences in thermal properties with surfactant type.

We have seen that increasing surfactant quantity lowers foam density. Lower foam density gives lower lambda values! Why? Our view is that the surfactant controls the amount of blowing agent that is captured – the more that is captured, the lower the foam density; the more that is captured, the lower the thermal conductivity. Ultimately, the more BA that is captured, the lower the cost of the formulation!

Polyol Effects:

Since ecomate is such a good a solvent for all foam raw materials, the original expectation was that it would solubilize all types of polyols equally; If this were so, polyol type would have little if any effect on solubility and ultimately on thermal conductivity. We set up a designed experiment to examine the effects of a combo of three polyols often used in spray foams [Table 5]:

Table 5	Functionality	Eq Wt	Viscosity	LO – HI LEVELS
Sucrose /Glycerin	7	152	30,580	25-75
EDA	4	70	17,310	0-25
ESTER	2.3	212	12,000	0-50

All formulations were designed to have the same amount of surfactant, catalyst, blowing agent, and were foamed at a 120 Index. We monitored density and thermal conductivity. The results of the 8 runs are shown in Figures 6-7.

Triangular graphs may be foreign to some readers. Let me explain how they work: The lowest amount of each polyol is shown as the base opposite the apex labeled for that polyol. The total amount dedicated to each polyol in this graph is 75 % [0-75% for ester and for EDA, and 25-100% for the sucrose/glycerin polyol]. But since in a mixture there can only be 100% total polyol, the active space is but a fraction of the entire graph. So, as indicated in Table 5, the EDA polyol ranges from 0-25% of the mix, while the other polyols make up the rest. So, in figure 6, the EDA polyol ranges from 0% to 25% [the remainder (25 – 75% to the apex for EDA is dark and not of concern in the experiment)], the ester ranges from 0% to 50%, and the sucrose/glycerin from 25% to 75%. The experimental space is then examined for statistically significant trends.

DESIGN-EXPERT Plot

DENSITY

● Design Points

X1 = A: SUC-GLY

X2 = B: ESTER

X3 = C: EDA

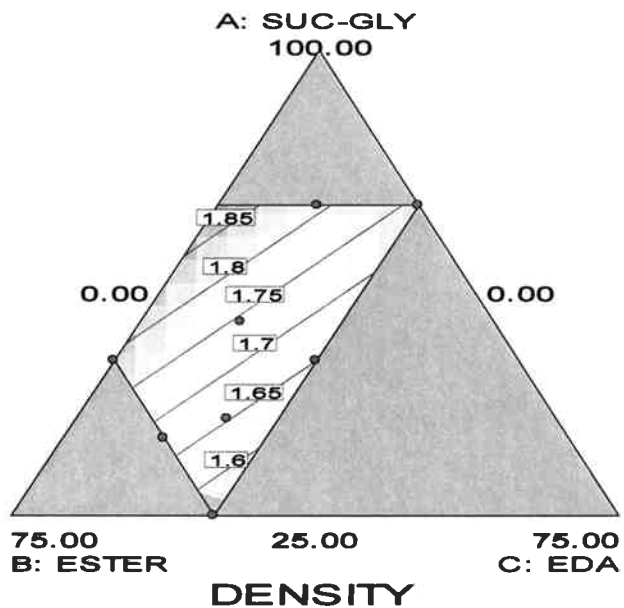


Figure 6: Effect on density

The effect on density seems directly related to the speed of the system [higher EDA content makes the formulation faster despite having the same catalyst amount in each foam]. Faster foams capture more BA, hence the lower density.

DESIGN-EXPERT Plot

THERMAL

● Design Points

X1 = A: SUC-GLY

X2 = B: ESTER

X3 = C: EDA

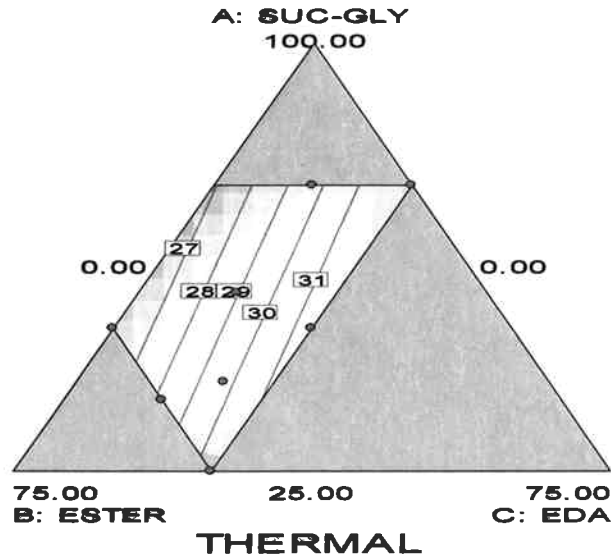


Figure 7: POLYOL TYPE on THERMAL PROPS

However, the thermal properties chart [Figure 7] demonstrates that the type of polyol can make a huge [and statistically significant] difference in the results obtained. Here one can see that an increasing quantity of EDA polyol seems to worsen thermal conductivity. This seems to contradict what we have said above, i.e., that faster systems should have lower thermal conductivity. A possible explanation: some types of polyols have such good solubility for MF that they absorb it from the cell vapor space into the foam matrix [windows and struts] at a very rapid rate. This is corroborated by work done by Moore⁵, et al, who state that polyol type and gel time are much stronger influences on foam k-factor than was the blowing agent level.

Catalyst Effects:

As mentioned above, the speed of the reaction and the orientation of the cells will affect the thermal conductivity. The catalyst propensity to blow or gel a given reaction will affect the cell geometry. Foam that gels prematurely will stretch and produce elongated cells. Faster foams generally have smaller, finer cells which contribute to improved thermal values.

Blowing Agent Effects:

We have shown thus far that the blowing agent is but a part of the thermal picture. But it does play a role. Of course, we all know of the dependence of k-factor on temperature; i.e., the lower the temperature, the lower is the k-factor [until the BA reaches its condensation point] [Figure 8]. This is precisely why thermal values should be determined in 'at use conditions', and why temperature is a necessary part of the k-factor or lambda value. Gaseous BAs tend to be linear over the course of use temperature; liquids [red line] tend to have a flatter curve after condensation set in.

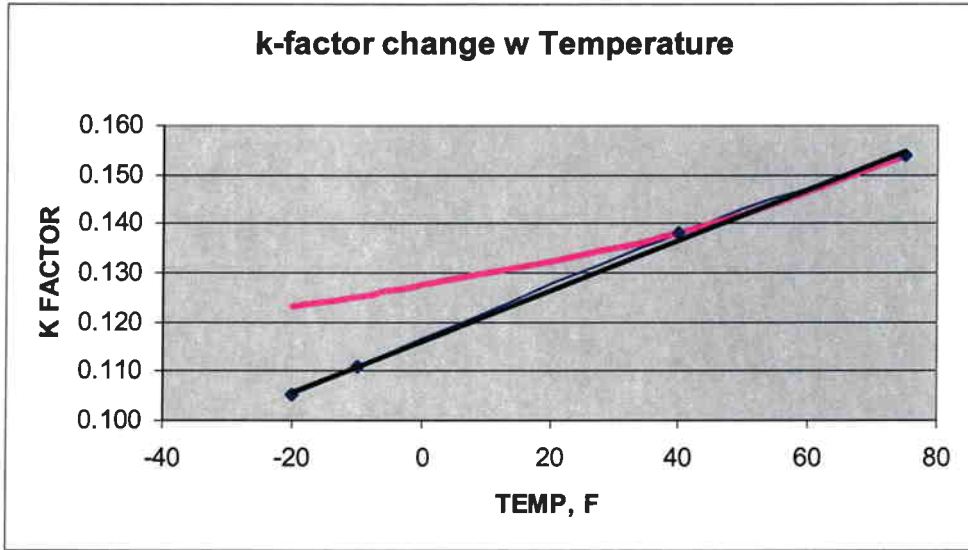


Figure 8: Gaseous BA [black] v Liquid BA [red]

Blowing Agent Loss:

Allow me to relate anecdotally an episode that happened to me many years ago. A sample of spray foam taken from a roof failure [coating had weathered off, allowing the foam to badly discolor and become laden with water] was tested for thermal conductivity. This apparent 2.5 pcf foam tested at $k = 0.25$. The foam was then placed in a 100 F oven for a week to dry it out, and it retested at 2.0 pcf and with a k-factor of 0.11. Exactly what it had been the instant it was manufactured! This strongly suggested that *CFCs have a much harder time getting out of foam than do moisture and atmospheric gases in permeating into the foam simply due to the relative size of each*. In fact, our industry warns against placing foams below grade level specifically because of the potential uptake of moisture into the foam.

Recent studies⁶ by AHAM [Table 6] have also shown that fluorinated BAs do *not* leave refrigerators over the course of the refrigerator life time [15-20 years]. If the blowing agent remains in the foam, *the major reason for K-factor drift is moisture invasion!* If we are truly concerned about thermal conductivity, we must protect PUR and/or PIR foams from atmospheric gas [especially water vapor] intrusion.

Sample	When Produced, Pre-1993	At End of Life, Prior to Shredding, 2004
A-1	15.2 %	15.4 %
A-2	14.1 %	13.0 %
B-1	15.9 %	16.0 %
B-2	16.7 %	15.2 %
C-1	16.0 %*	16.0 %
C-2	13.0 – 14.0 % *	13.8 %
D-1	14.0 – 16.0 % *	15.7 %
D-2	14.0 – 16.0 % *	14.3 %

* - estimate; exact records not available

Blending BAs:

Since ecomate is so very compatible with other BAs on the market, it is natural to consider blending it with another BA to improve the properties of both. In Table 7 we show a series of experiments using ecomate blended with HFC-245fa [a gaseous BA] in the same polyol system [same surfactant, catalyst, etc].

The addition of the HFC does lower thermal conductivity of the foams made, but there is a small loss in cold dimensional stability with increasing HFC content. Thus there is a price to pay in using this HFC. One must always ask 'Is it worth the additional cost and the slightly poorer physicals to gain a small amount of thermal conductivity?'

Table 7		96-1	96-2	96-3	96-4
Ecomate, mol%		90	75	50	25
HFC245fa, mol%		10	25	50	75
K-factor, init		0.165	0.161	0.158	0.153
CS//		31	25	33	24
Dim Stab Cold, 28d		2	3	5	9

RESULTS

In conclusion we summarize our work -

1. In our drop-in study HFC 245fa and ecomate are nearly equally efficient.
2. Hand mix studies are always inferior to machine mixed.
 - a. Better mix = lower lambda;
 - b. Higher surfactant levels are better
 - c. Larger pours [diminished surface area of pour] = better;
 - d. Higher surfactant level effect is lost at low mixer speed.
3. Processing Effects
 - a. Machine mix is always better;
 - b. Lower density is better;
 - c. Cell orientation important
 - i. Long cells = poorer lambda
4. Formulation Effects
 - a. Surfactant type and amount are critical
 - i. Captures more BA
 - ii. Lowers density
 - iii. Improves lambda
 - b. Polyol type is also very important
 - i. Affects lambda as well as other physicals
 - c. Catalyst affects cell size and orientation;
 - i. Orientation critical
 - ii. Smaller cells better
 - iii. Faster is better
 - d. Worry little about BA loss
 - i. Protect foams from atmospheric moisture;
 - e. Blends with ecomate possible and good
 - i. Must weigh benefits

CONCLUSIONS

We have covered much ground in this paper. Presented here are many formulation and application techniques that can enhance the thermal properties of a given system, and save money in doing so. The thermal properties of a foamed product DO NOT EXCLUSIVELY depend upon the thermal conductivity of the physical blowing agent used, but also on the way the foam is formulated, on the way the foam flows, and on the way the foam is protected after it is foamed. As the available blowing agent choices become fewer, and their molecular weight becomes smaller, it behooves the formulator to take at least some of the steps shown here to insure that he achieves optimal thermal conductivity from his foams. If one is truly serious about thermally efficient foams, not just using k-factor or lambda values as a sales tool, one will take steps to protect their products from atmospheric moisture.

REFERENCES:

-
- ¹ J. Murphy, M Schulte, and B. Green, "ecomate® Foam Blowing Agent", Polyurethanes Conference Proceeding, p302, 2005.
 - ² J. Murphy, "ecomate® - a multi-faceted Blowing Agent", Polyurethanes Conference Proceeding, 580, 2006.
 - ³ J. Murphy and D. Jones, "The Revolutionary Blowing Agent for Europe", 18, 2006
 - ⁴ C. Eilbracht and P Hohl, "Tailored Surfactant Solutions to Optimize Foam Performance in HFC-245fa Blown Appliance Systems", Polyurethane Conference Proceeding, 341-349, 2004
 - ⁵ S. Moore, C. Martin, and B. Obi, "Improving Initial HFC-245fa Foam Offerings for the Rigid Appliance Industry", Polyurethanes Conference Proceeding, 156, 2004
 - ⁶ L. Wentje, AHAM study on regrinding refrigerators, 2006

BIOGRAPHY

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.

