Improved Insulation for Commercial & Domestic Appliances

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ABSTRACT

There is both economic and environmental pressure on the Appliance Industry to produce appliances that are energy efficient as well as non-damaging to the environment. The choice of foam blowing agent plays a major role in the efficiency of the appliance and upon its impact on the environment both now and in the future [a legacy of encapsulated BAs and ever tighter restrictions]. The change from CFC to HCFC to HFC has had its challenges, both in efficiency and particularly in cost. HFE conversion will also lead to high cost insulation.

This paper will show how the patented blowing agent ecomate®[1,2] can improve the environmental impact of these appliances while achieving all the other criteria requisite for superior appliance manufacture: good fill properties, good dimensional properties and good thermal properties. Finally we will demonstrate the cost and environmental savings that can be had with ecomate blown foams with improved Energy Star ratings.

INTRODUCTION

The Domestic Appliance Industry in the US continues to be challenged by its need to produce appliances that are energy efficient as well as non-damaging to the environment, and to do this economically. The thermal efficiency of a refrigerator is dependant mainly on the choice of foam blowing agent selected, and in the system in which it is used. The onus of Ozone Depletion initially forced a change from CFC-11 to HCFC-141b, and Global Warming worries prompted a second change to either hydrocarbons, such as the pentanes, or to HFCs [such as HFC-245fa]. All the while blowing agents choices have become more expensive, and at the same time less thermally efficient.

In addition, while these transitions are taking place in developed countries like the US, manufacturers in other countries who did not have to make the transition are allowed to import their products into the US, unfairly competing with their more efficient, less costly units.

COMPETITION - PRESENT AND FUTURE

While there is mounting pressure to transition the less developed countries over to HFCs or other BAs, there is similar pressure mounting to curtail the use of HFCs in the US. Why? Because HFCs, as improved as they are, still contribute to global warming, and also because it has recently been discovered that HFCs are stable enough NOT to decompose in landfills at the end of the refrigerator lifetime. Thus the units produced today with HFCs are immediately becoming a legacy for our sons & daughters.

What about HFE and HFOs? They are not immediately available because of ongoing toxicity testing and needed production scale-up. We have been told that they might be available in late 2010 to early 2012. What do we surmise these molecules are, and what might they cost?

Future potential BAs are described in Table 1.

These potential next generation BAs may eventually come to market, if they pass toxicity testing. Although we do not yet know the exact properties of each of the molecules, we do know that the HFOs [hydro fluoro-olefins] <u>below</u> can be readily made from HFC-245fa[3]. It is likely that AFA-L1 could be made from HFC-365mfc, by a similar process. FEA-1100 is more likely an ether, rather than an olefin.

TABLE 1: Potential New BAs [4th Generation]

	FSI	DuPont	Honeywell / DuPont	Honeywell	ARKEMA
	ecomate	**FEA1100**	**HFO1234yf**	**HBA1 HFO1234ze**	**AFA-L1**
	HCOOCH3	CF3CF2CH2-0-CH3	CF3CF=CH2	CF2H-CH=CF2	CF3CH2CH=CFH
MW	60	164	114	114	128
normalized MW	1	2.7	1.9	1.9	**2.1**
# F	0	5	4	4	4
%F	0	58%	67%	67%	59%
BP, ºC	32	25	-29	<-15	<30>10
Lambda	10.7	10.7	13 ?	13	10
FLASH PT, C	-32	NO	NO	NO	NO
LFL	5	NO	NO	NO	NO
UFL	23	NO	NO	NO	NO
ODP	0	0	0	0	0
GWP	0	5	4	6	<15
VOC	EXEMPT	**?**	**YES?**	**YES?**	**YES?**

While these blowing agents have much improved GWP values, they still have some drawbacks. First, they likely will be more expensive than the already costly HFCs they are replacing. Combined with their high molecular weight, the overall cost will reduce their attractiveness to potential users. They are unlikely to obtain VOC exemption because of the presence of unsaturation. Unsaturated molecules usually have much higher MIR (maximum incremental reactivity) values relative to the creation of smog. It does not seem advisable to trade one environmental problem for another. The cost to be non-flammable seems too high.

To be an acceptable blowing agent for this industry, the foam made from it has to have good physical properties, especially thermal properties. The thermal properties of a neat blowing agent [lambda, above] are only an indication that the BA might perform adequately. Because of this, the industry usually requires that several units be made and tested by a procedure called a Reverse Heat Flow Analysis to ascertain its ability to insulate adequately, independent of the compressor. More on this later.

Besides the establishment of good thermal properties, this industry requires the BA to obtain GRAS [Generally Recognized As Safe], a legal opinion based upon a large amount of testing that if the blowing agent should leach through the foam and the plastic inner liner of the refrigerator and be absorbed into the food inside, that it would be in low enough concentration [or have low enough toxicity] to be of no consequence to humans. This testing, and the subsequent publication in a peer reviewed scientific journal may well take over a year. To say nothing of cost!

Some manufacturers have transitioned to pentanes to blow their foams in order to maintain a competitive stance with HC and HCFC imports. This transition comes with an acceptance of flammability, and the requisite process changes to use flammable BAs. And very often this transition requires an acceptance of poorer lambda values. Fortunately, in July of this year the importation of products containing HCFC-141b will cease, allowing domestic manufacturers to better compete against foreign imports.

ENTER ECOMATE

While ecomate [neat] is flammable, it is far less flammable than HCs. This has been documented in many previous papers (4) . When blended into polyol [or isocyanate], it can be handled in the same way as 141b. It has almost identical properties, such as boiling point, solubility and flammability.

Before investing heavily in obtaining GRAS approval, we thought it prudent to demonstrate to this industry the benefits that ecomate use can bring. First of all, ecomate has been approved at one of the major Drink Dispenser manufacturers in the country. It [ecomate] provided superior flow and fill properties to the previous 134a based system, and the insulation properties were identical as measured by side-by-side ice melt testing [Figure 1].

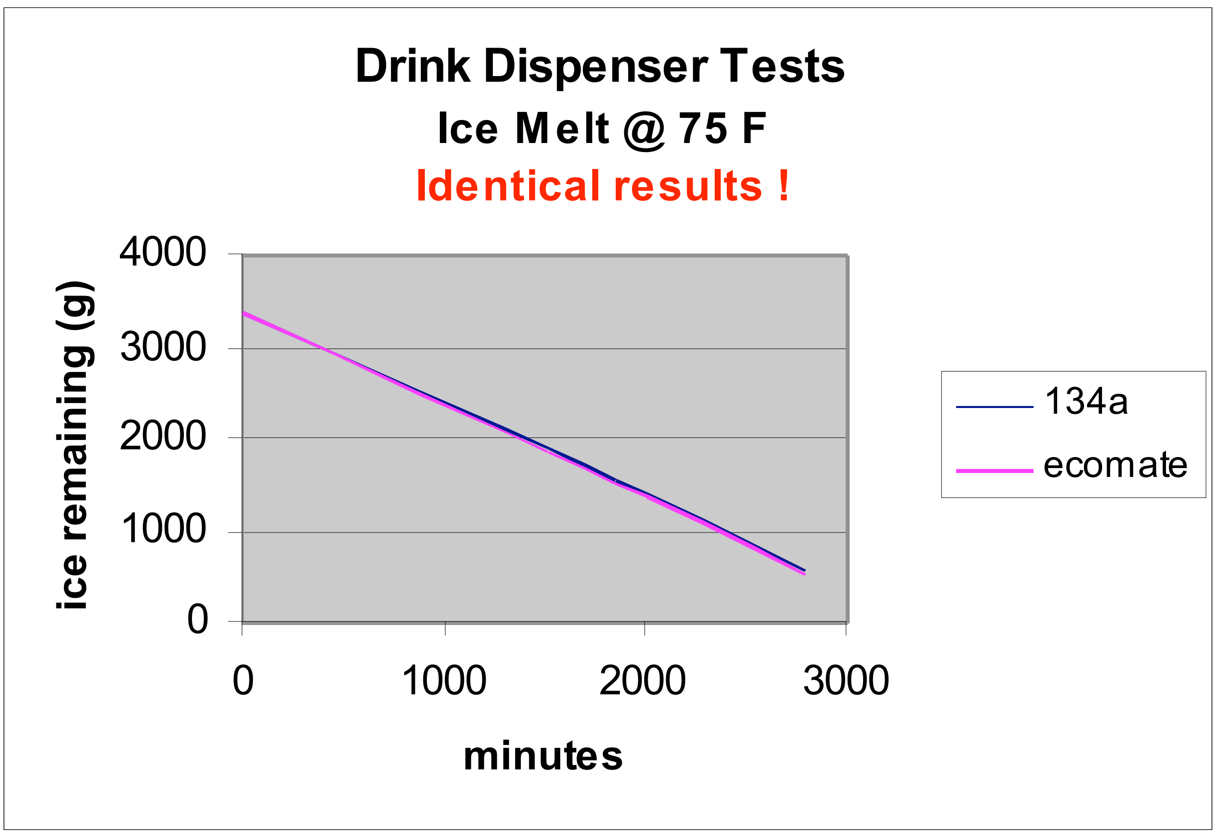

Figure 1: Drink Dispenser Ice Melt Tests at 75°F – 134a v ecomate blown insulation

It is also achieving marked success in display cases and commercial refrigeration, getting identical results as foamed units blown with 245fa. For example, an industrial refrigeration manufacturer adopted ecomate blown foam in its latest cabinets and surpassed Energy Star requirements by 23.7%.

Another commercial appliance manufacturer, when faced with the proposition of changing to 134a blown foam when R22 was phased out, decided instead to convert to ecomate blown systems because of its efficiency and low environmental impact. They achieved the same insulation values at the same thicknesses as the original products, and used 10% less foam.

Figure 2: Commercial Fridge besting ENERGY STAR requirements by 23.7%

Inspired by this success, a supplier to the domestic refrigeration market was approached to build a number of units foamed with ecomate blown foam. The unit selected was a 7 cubic foot freezer chest.

The dimensions of the unit are shown in Table 2a. The nominal 7 cu. ft. unit was only 6.67 cu. ft, and required 9.5 pounds of foam at a targeted 2.13 pcf core density. The foam was dispensed in 3.23 seconds through a 40 ppm High Pressure machine. Demold was 2.5 minutes after shot time.

Table 2a: Ecomate Chest Dimensions

ECO	ID	OD
L	26.5	31.5
W	16.25	22.75
H	28.75	31.75
COMPRESSOR WELL		
L	9	
W	9	
H	10.5	
CU FT	6.67	13.17

Table 2b: 141b Chest Dimensions

141b	ID	OD
L	31.5	37
W	15.125	20.75
H	27.5	31
COMPRESSOR WELL		
L	7.5	
W	7.75	
H	20.75	
CU FT	6.88	13.77

In order to do a modified Reverse Heat Flow test, a second commercial unit from the same supplier was purchased from a local hardware. Its dimensions were not quite the same [Table 2b], and we then learned that it was made in China and its **foam blown with 141b**. Not a true side by side comparison, since no current foam blowing agent can equal the gas lambda of 141b [10 v 10.7 for ecomate]. Undaunted, we pressed on.

In the first test, the units were placed inside a walk-in refrigerator, maintained at 42ºF.

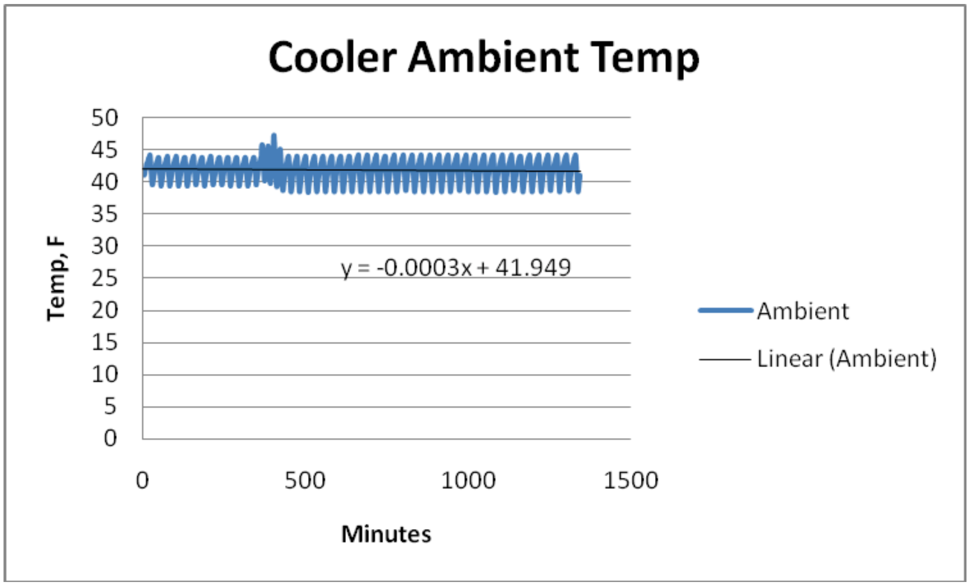

Figure 3: Ambient Cooler Temp [42 ºF] for Reverse Heat Flow testing.

Heat was generated inside the boxes by a transformer controlled [to 89.9 volts] 40 Watt light bulb. Temperatures inside both units and inside the cooler were monitored with 3 **EXTECH RHT10** temperature probes [one for each unit and one for the ambient cooler]. We monitored the units once each minute for 70 hours.

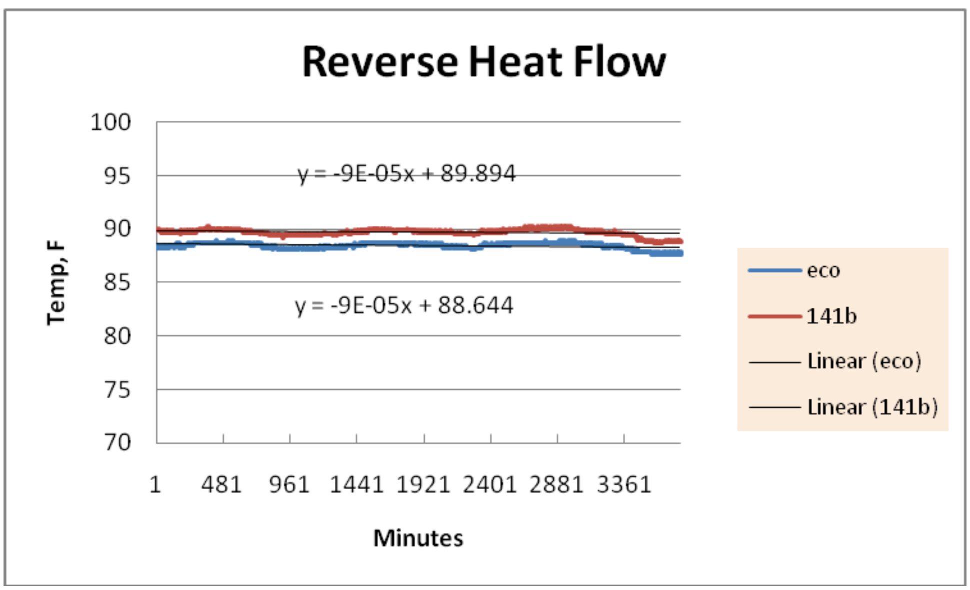

Figure 4: Reverse Heat Flow of ecomate- and 141b- blown Freezer Chests

While there is some variation in the minute to minute readings of each box [which follows the cyclic variation in the electricity supply during each 24 hr period, thus affecting the wattage of the bulbs used], the trendline shows that both units have the same slope and differ only by the average temperature they held over those 70 hours:

- 141b blown foam = 89.894ºF
- Ecomate foam = 88.644ºF
- A difference of **1.25ºF, or 0.7 ºC**

We then decided to place the two units in a Cold Storage Freezer maintained at 0ºF [Figure 5]. The ambient temperature in the freezer shown in this figure averaged negative 1 degree F. The chests under test were heated in the same manner, this time using 100W bulbs. An attempt was made to get the interiors of the freezer chests once again to 90ºF, but we fell slightly off the mark [Figure 6]. The rheostat was set at 75% in this trial. With a delta temperature this time of almost 90ºF, the chests again did remarkably well:

- 141b blown foam = 86.007ºF
- Ecomate foam = 84.735ºF
- A difference of **1.27 ºF, or 0.7 ºC**

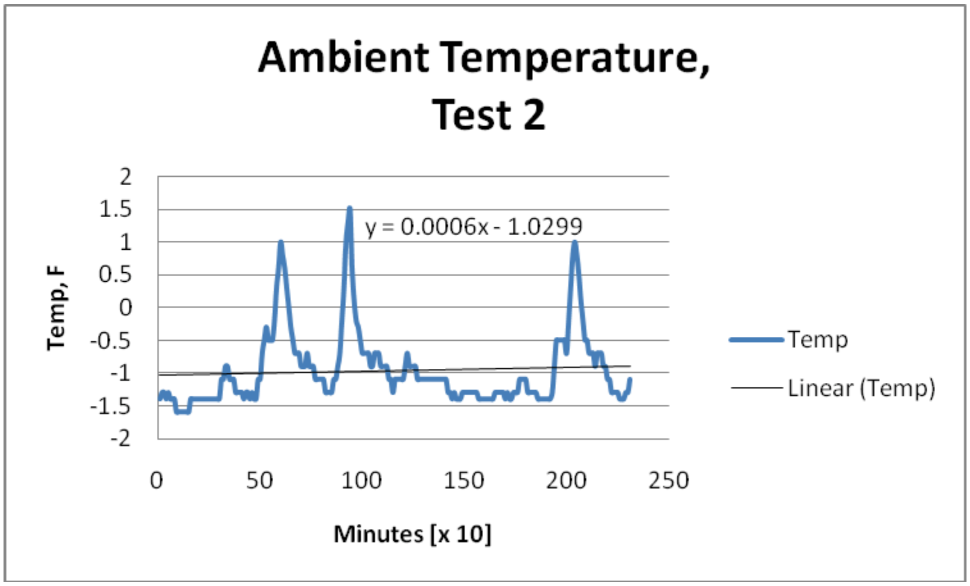

Figure 5: Ambient temperature of Zeroº F Freezer used in Test 2

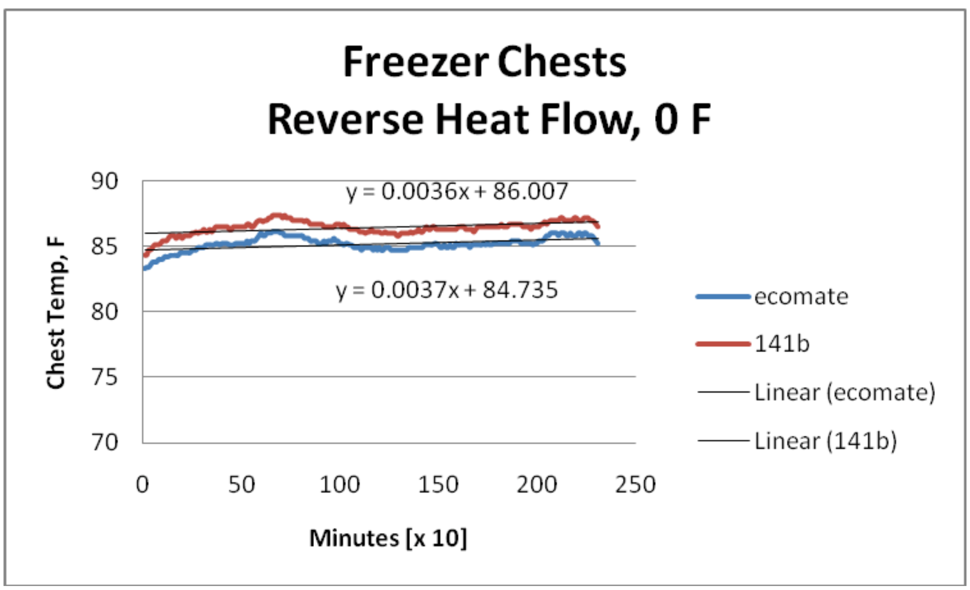

Figure 6: Reverse Heat Flow of ecomate- and 141b- blown Freezer Chests at Zeroº F

While elated at the excellent performance [*identical results at two different temperatures*] of the ecomate blown system against that of the HCFC-141b blown chest, we know that there were several deficiencies in the formulation we investigated.

Having no previous experience with domestic refrigeration formulations, this formulation was in no manner optimized. In our first effort, our reaction rates were slow [in fact, we adjusted reactivity at the demo], our densities high, and our closed cell content low. This lack of optimization resulted in poorer than expected thermal conductivity.

The thermal conductivity of a urethane foam is a result of the thermal conductivity of the blowing agent certainly, but also of the polyurethane matrix – the fineness of cells and their orientation. The finer the cells, the better the insulation. And the faster the reaction rate, the finer the cells. However, faster reactivity may prove to be a challenge in terms of processability, particularly resulting in reduced flow and elongated , stretched cells. Our formulation [Table 3], while finally having the required reactivity, did not have the flow parameters [flow index and core/fill ratio] it needed, nor the closed cell content. In spite of these deficits, we feel it did very well in the reverse heat flow tests.

Table 3: System Properties of foam used

Run Summary	Req'd	S1a
Gel	35-40	35
Tack Free	55-65	55
Free Rise Dens, pcf	1.40	1.42
LANZEN PANEL		
MFD, pcf	1.94	1.98
Flow Index [MFD/FRD]	1.38	1.40
Physicals		
Core Density	1.8	1.8
Core/Fill Ratio	0.90	0.80
Closed Cell Content	90% min	87.4
K-factor @75°F	0.137	0.166
@50°F	0.127	0.156
Dim Stab 14d @ -25°C	<-2%	-1.42

We have recently done work in-house with ecomate foam formulations and have achieved the requisite thermal properties listed above and are anxious to put these formulations to the test. And with this confidence, we are pursuing GRAS status for ecomate.

Ecomate affords the formulator economies of cost. With the lowest MW of any commercial blowing agent, and with pricing similar to hydrocarbons, the usage levels will be low and the pricing right. It offers economy of production, since no expensive plant conversions will be required for its implementation. It offers environmental economy as well, since for every pound of ecomate used to replace an HFC, over one metric tonne [2200 lbs] of CO2 equivalents can be saved. And best of all, ecomate performs. … we have had loyal customers successfully using ecomate for the past decade.

CONCLUSIONS

1. The next generation of HFEs or HFOs are still probably 2 years away. They will be as expensive as the HFCs they are made from. They may be flammable, and may be smog producers. Toxicology is pending.
2. Ecomate is here today! It is efficient, cost effective, and benign to the ecology. It leaves no legacy to the environment.
3. Ecomate gives very nearly same reverse heat flow results as did 141b, both at refrigerator and freezer temperatures, without being formulation optimized.

FOOTNOTES

(1). Ecomate® is a registered trademark of Foam Supplies, Inc. for methyl formate foam blowing agent.

(2) (a) **US 6,753,357**, "Rigid Foam Compositions and Method Employing Methyl Formate as a Blowing Agent," Kalinowski, Timothy T., et al., June 22, 2004.
(b) **Australia Patent 2002357892** "Rigid Foam Compositions and Methods Employing Alkyl Alkanoates as a Blowing Agent." Schulte, Mark S., et al. Issued Aug.17, 2006.
(c) **Singapore Patent 104780** "Rigid Foam Compositions and Methods Employing Alkyl Alkanoates as a Blowing Agent." Kalinowski, Timothy T., et al. June 30, 2005.
(d) **South Korea patent 10-0649377**, "Rigid Foam Compositions and Methods Employing Alkyl Alkanoates as a Blowing Agent." Kalinowski, Timothy T., et al. Nov. 17, 2006.
(e) **Mexican Patent (**No number issued at this point. **Appl. No. 2006/010120)**. "Rigid Foam Compositions and Methods Employing Alkyl Alkanoates as a Blowing Agent" Kalinowski, Timothy T., et al. Feb. 20, 2009.
(f) **Mexican Patent 242616** Rigid Foam Compositions and Methods Employing Methyl Formate as a Blowing Agent. Kalinowski, Timothy T., et al. Dec. 11, 2006.
(g) **South Africa Patent 2007/00963** Reactivity Drift and Catalyst Degradation in Polyurethane Foam. Schulte, Mark S., et al. Oct. 29, 2008.
(h) **Chinese Patent** in 2009. Number not available at this time.

(3). US Patent Application 20050247905, Honeywell Corp.

(4) (a) Murphy, J. A, 2008 "Ecomate - Environmentally Benign Foam Blowing Agent", Presented at the American Chemical Society's 12th Annual Green Chemistry & Engineering Conference, Washington DC, June 26, 2008
(b) Murphy. J, Schulte, M, and Green, B. 2005 *POLYURETHANES Technical Conference* '05 "Ecomate Foam Blowing Agent", 302-309
(c) Murphy, J. 2006 *POLYURETHANES Technical Conference* '06, "Ecomate – a multi-faceted Blowing Agent", 580-587
(d) Murphy, J. 2007 *API POLYURETHANES Technical Conference 2007*, Energy Critical Foams - Paper 8 "Factors contributing to k-factor optimization with ecomate blown foams"
(e) Murphy, J. 2008 API *POLYURETHANES Technical Conference* 2008, Insulation Options – paper 58, "A Comparison Of Physical Properties [and their causative factors] Of Froth v Pour Foams"
(f) Murphy, J, Jones, D. 2006. "The Revolutionary New Blowing Agent for Europe", presented at the 2006 Utech Conference Paper 18
(g) Murphy, J. 2009. "Environmentally Benign Foam Blowing – the time has come", presented at the 2009 Utech Conference, paper 43
(h) Murphy, J, Jones, D. 2009. "Environmental Advantages of Pentane and NIK Blends", presented at the 2009 Rapra Conference, Paper 202

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.