
Long-term Aging of Closed-Celled Foam Insulation

John Murphy

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

ABSTRACT

Many factors influence the thermal efficiency [lambda value or k-factor] one obtains with foams blown with any of the commercial physical blowing agents. Factors affecting a product's thermal efficiency depend on, but are not limited to, the blowing agent itself – such items as the blowing agent's molecular weight, its boiling point, and 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. Still 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.

The long-term aging of foams has always been filled with myth and controversy. This has been true for every blowing agent that has been commercialized. We will try to dispel some of the myths with the results of several long-term aging studies, run on ecomate® and other commercial Blowing Agents.

INTRODUCTION

Allow me to relate anecdotally an episode that happened to me many years ago that caused me to start thinking about this issue. 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 pounds per cubic foot (pcf) [40 kg/m³] density foam tested at $k = 0.25 \text{ BTU-in/(hr)(ft}^2\text{)}(\text{°F})$ [36 mW/m K]. The foam was then placed in a 100 °F [38 °C] oven for a week to dry it out, and it retested at 2.0 pcf [32 kg/m³] and with a k-factor of 0.11 BTU-in/(hr)(ft²)(°F) [15.8 mW/m K]. Exactly what it had been the instant it was manufactured!

jmurphy@foamsupplies.com

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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 [MW] of each. In fact, our industry warns against placing foams below grade level specifically because of the potential uptake of moisture into the foam.

In this paper we try to differentiate the effects of moisture infusion versus blowing agent diffusion by means of previous literature studies, our own experiments, and long-term aging studies. In one study, the 5+ year drift of ecomate blown insulation was monitored on the same unit under the same conditions.

AGING – MYTH OR FACT?

The truth of Foam Aging [or more succinctly, the loss of thermal insulation efficiency with time] seems certain. Most of us have seen it happen to our foams. Many prestigious research labs [such as ORNL⁽¹⁾] have investigated the phenomenon. There have been many papers written on the subject over the years. Many countries, including the US [ASTM C-1303⁽²⁾] and Canada [CAN/ULC S-770⁽³⁾], have adopted test methods on how to measure this change.

What are the consequences of this aging? Quite succinctly, it amounts to a loss of trust in our industry by the public, and potentially by the government. If the thermal insulation value [so anticipated, and so critically important that one goes to the expense of putting urethane foam insulation in place], is slowly dissipating, how do we as an industry advertise the *true* insulative efficiency of the foams we produce? How do we likewise maintain credibility regarding the principle item we sell – insulation? We need to better understand the aging process.

So if foams age, why do they age? The common belief is that the blowing agent [BA] diffuses out of the foam over time.

While this may in part be true, this author believes it to be surrounded in MYTH. The purpose of this paper is to give various types of evidence to show that the perceived “aging” of foams centers upon the infusion of moisture laden air into the foam.

The crux of the situation and the real challenge here is:

How does one effectively differentiate the effects of moisture infusion from those of BA diffusion?

LITERATURE EXAMPLES

1.1 DuPont Study

A paper published in 1986 by Baitinger *et al.*⁽⁴⁾ [DuPont], discussing the aging of Polyurethane foams does just that. In their study, they wrote:

“Thermal conductivity testing of the PUR production board was performed at two different laboratories using different test equipment and aging conditions. Canadian measurements were done on an ANACON k-factor Instrument; the faced boards sections were cut into six inch squares and the facers removed just prior to k-factor testing. For the accelerated aging, faced 18”x18” sections with edges exposed were stored in an oven for 28 days at 80 °C.”

“The US thermal conductivity tests were done in accordance with ASTM C518 using a Dynatech K-Matic Instrument. The board product samples were cut into one foot squares and the foil facers removed just prior to k-factor testing. For the six month ambient aging two 4’x4’ boards (half sections) were stored in a well ventilated and heated/air conditioned area. The other 4’x 4’ sections of each board were used for the initial k-factor measurements. The 1’x1’ squares with facers removed, used to obtain the initial values, were retested after 6 months storage for control purposes. These unfaced squares showed typical aging after 6 months while the faced board showed no significant change. These k-factor results are shown in **Table 1.**”

Table 1*. Foil faced PU production board k-factor aging tests in BTU-in/(hr)(ft²)(°F)

| Sample | Initial | Canadian Test Conditions After 28 Days, 80 °C |
|----------------------------------------|---------|--------------------------------------------------|
| Epoxy Coated Foil - PUR | 0.128 | 0.128 |
| ACR Coated Foil - PUR | 0.128 | 0.129 |
| Sample | Initial | US test conditions after 6 months, 70 °F, 50% RH |
| ACR Coated Foil - PUR | 0.129 | 0.133 |
| Foil facer removed | | 0.163 |
| <i>*Baitinger et al.⁽⁴⁾</i> | | |

As stated by the authors, the samples aged in the 80 °C oven one month did not drift. The ambient [70 °F/50%RH] materials stored with foil facers in place drifted only slightly, while the foams with Al facers removed fared poorly. This data clearly shows that if the foam board is kept dry, the increase in thermal

conductivity is negligible. Thus, if foam is exposed to moisture [even as low as 50% RH] its thermal conductivity will climb dramatically.

1.2 NRCC Study

In another literature study, Dr Mark Bomberg⁽⁴⁾, National Research Council Canada concludes: “the greatest loss of thermal resistance results from the diffusion of air [moisture] into the cells...the loss of blowing agent from outward diffusion is not a major factor in the reduction of thermal resistance of the insulation.”

1.3 AHAM Study

Is there documented proof that the Blowing Agent stays in the foam? Recent studies⁽⁵⁾ by AHAM [**Table 2**] have shown that fluorinated blowing agents 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!

Table 2. Amount of CFC-11 blowing agent in sampled refrigerators⁽⁶⁾

| 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

1.4 Huntsman Study

Dr Singh *et al.*⁽⁷⁾ [Huntsman] in developing their **Agesim** software, studied the aging characteristics of polyisocyanurate [PIR] laminate foams blown with water and a combination of cyclopentane [cC₅] and isopentane [iC₅]. They aged lambda blocks [12"x12"x1"] at well defined temperatures, and did cell gas analyses on core samples of foam to determine the effective diffusion

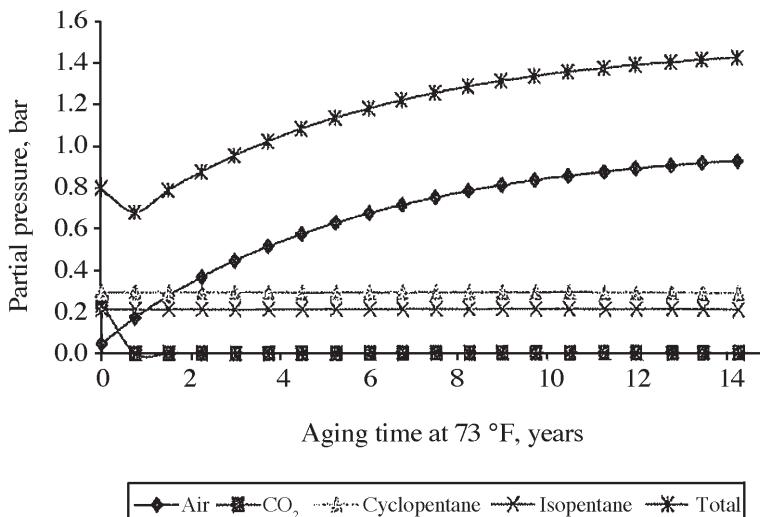


Figure 1. Predicted 15 year change in blowing agent partial pressure at 73 °F (23 °C) – Board #2 of Singh *et al.*⁽⁷⁾

coefficients [D_{eff}] of the cell gases. With this information and their Agesim algorithms, they predicted [Figure 1]⁽⁷⁾ that:

- CO_2 [formed by reaction of water with the isocyanate] rapidly diffuses out of the foam,
- The hydrocarbons, $i\text{C}_5$ and $c\text{C}_5$, remain in the foam, and
- The predication factor to foam aging is the infusion of air over time.

MATHEMATICAL ARGUMENTS

Let's examine the practice of thin slicing to predict the aging of foam. A foam sample is cut into equal thin slices to mathematically determine the rate of blowing agent release - the thinner the slice, the faster the aging. Seems logical – thinner sections, with more surface area, beget faster diffusion. But diffusion of what, one might ask?

Physical blowing agents rely on their boiling point, their solubility in the polyol, and their gaseous thermal conductivity to be useful as BAs. They are used on a molar basis – equi-molar quantities will give the same density of foam.

Table 3. Molecular weights and boiling points of some historic blowing agents

| BA | MW | BP, °C |
|------------|-------|--------|
| CFC-11 | 137 | 23.7 |
| HCFC-141b | 117 | 32.2 |
| HFC-245fa | 134 | 15.3 |
| HFC-365mfc | 148 | 40 |
| ecomate | 60 | 32 |
| | | |
| CFC-12 | 121 | -29.8 |
| HCFC-22 | 86.5 | -40.8 |
| HCFC-142b | 100.5 | -9.3 |
| HFC-134a | 102 | -26.2 |

But the molar weights of BAs have been quite different over the short history of PU foams [Table 3]. Their diffusion rates must be equally divergent. And if these liquids and /or gases are trying to get out of the foams, what is trying to get into the foams? Atmospheric gases, of course! Graham's Law [Equation (1)] states that the rate of diffusion of given gases is inversely proportional to the square roots of their MWs. Which are the atmospheric gases, what are their concentrations, and their MWs? See Table 4.⁽⁶⁾

The data in Table 4 shows the gas composition of *dry air* at sea level, but it completely ignores the percentage of water vapor in this composition. This can be obtained from Figure 2⁽⁷⁾, which suggests that there is between 2-2.5% in saturated air at RT at Sea Level. So, of all the common atmospheric gases, water is generally third in concentration and lowest in MW. At 50% RH and 25 °C, the absolute humidity is 11.5 g/m³.

Table 4. Standard dry air composition⁽⁸⁾

| Gas | Form | % by Volume | % by Weight | Molecular Weight |
|----------------|-----------------|----------------------|-------------|------------------|
| Nitrogen | N ₂ | 78.08 | 75.47 | 28.01 |
| Oxygen | O ₂ | 20.95 | 23.20 | 32.00 |
| Argon | Ar | 0.93 | 1.28 | 39.95 |
| Carbon Dioxide | CO ₂ | 0.038 (2006) | 0.0590 | 44.01 |
| Neon | Ne | 0.0018 | 0.0012 | 20.18 |
| Helium | He | 0.0005 | 0.00007 | 4.00 |
| Krypton | Kr | 0.0001 | 0.0003 | 83.80 |
| Hydrogen | H ₂ | 0.00005 | Negligible | 2.02 |
| Xenon | Xe | 8.7x10 ⁻⁶ | 0.00004 | 131.30 |

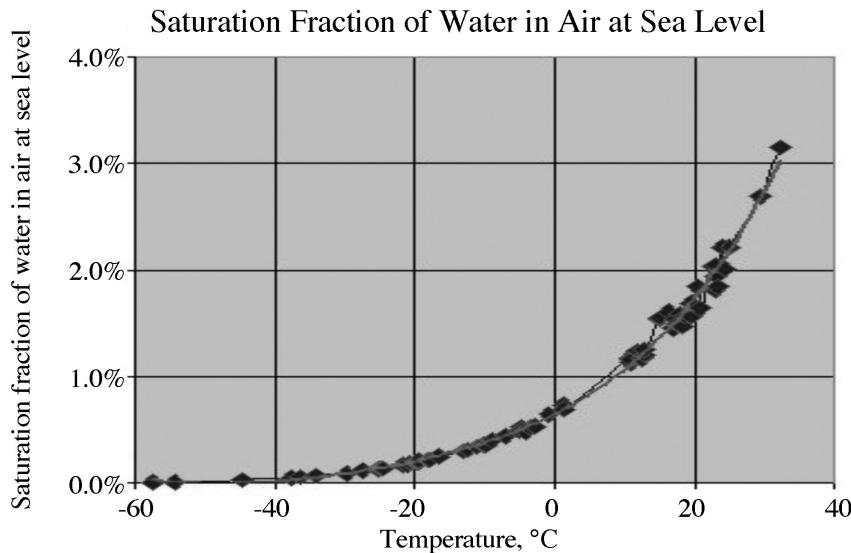


Figure 2. The standard fraction of water in saturated air at sea level⁽⁹⁾

This means that water [MW=18], Nitrogen [MW=28], and oxygen [MW=32] are trying to get into the foam at the same time as the BA is trying to get out. Nature always wants to reach a state of equilibrium! Water, being the smallest of these, will also be the fastest to diffuse [according to the diffusion rate for porous materials of Graham's Law]:

$$\frac{\text{Rate}_1}{\text{Rate}_2} = \sqrt{\frac{M_2}{M_1}} \quad (1)$$

Thus the diffusion rate of water = $\sqrt{(102/18)} = 2.38$ times the diffusion rate of HFC-134a, and the diffusion rate of nitrogen = $\sqrt{(134/28)} = 2.19$ times the diffusion rate of HFC-245fa, for instance (see Table 5). Thus water infuses at a rate 2-3 times that of most any BA diffusion, if the foams were porous. But they are not! Most rigid foams, whether they be PUR [polyurethane] or PIR [polyisocyanurate], have 90+% closed cells.

Table 5. Graham's Law diffusion comparison [calculated]

| | | 245fa | 365mfc | 134a | pentane | ecomate |
|----------|----|-------|--------|------|---------|---------|
| | MW | 134 | 148 | 102 | 72 | 60 |
| Water | 18 | 2.73 | 2.87 | 2.38 | 2.00 | 1.83 |
| Nitrogen | 28 | 2.19 | 2.30 | 1.91 | 1.60 | 1.46 |
| Oxygen | 32 | 2.05 | 2.15 | 1.79 | 1.50 | 1.37 |

There are many other parameters that must be considered, such as solubility in the polymer, fineness of cells, density of foam, and especially closed cell content of the foam - which means that Fick's Law must be invoked [a much more complicated calculation]. In one dimension, this is:

$$J = -D \frac{\partial \phi}{\partial x} \quad (2)$$

where

J is the diffusion flux, $\left(\frac{\text{mol}}{\text{m}^2 \cdot \text{s}} \right)$. J measures the amount of substance that will flow through a unit area during a time interval,

D is the diffusion coefficient or diffusivity $\left(\frac{\text{m}^2}{\text{s}} \right)$,

ϕ (for ideal mixtures) is the concentration $\left(\frac{\text{mol}}{\text{m}^3} \right)$,

x is the length (m).

Solving Equation (2) will show that the diffusion rate for water is over several 100x faster than some of the smallest commercial blowing agents currently on the market. For instance, using the diffusivity data of Hydrocarbon blown foams [shown in **Table 6** below] we see that:

- Different gases have different diffusion rates [$\text{CO}_2 > \text{Air} > \text{BAs}$];
- The Effective Diffusion [or diffusivity] is greatly affected by temperature – becoming faster with increasing temperatures;
- In addition, the processing conditions can also affect effective diffusivity, as seen by differences in boards 1 and 2 – which were essentially the same formulation run on two different lines.
- For HC blowing agents, the rates can be from $0.128/3.77 = [0.034] = 1/29$ to $0.073/40.3 = [0.002] = 1/552$; that is 29 to 552 times slower than air infiltration [**Table 6**]!

Size isn't everything! While the general trend is for better insulation values with increasing molecular weight [**Figure 3**], this loose generality is NOT the case with specific molecules [**Table 7**]. For example:

- The smaller molecule, HCFC-141b [MW 117], is a better insulator than larger HFC-245fa [MW 134] where $\Lambda = 10 \text{ mW/mK}$ versus 12 mW/mK , respectively; or

- Approximately equal sized molecules can be considerably different from one another. For instance, HFC-245fa [MW 134] is nowhere near as efficient as CFC-11 [MW 137] – (Lambda = 12 versus 8 mW/m K).
- On the other hand, ecomate® [MW 60] is nearly as efficient as HCFC-141b.

Table 6. Effective diffusion rate of gases in core foam of Boards 1 and 2; and comparison to the rate of air infusion into same foams

| Effective Diffusion | | | Rate of Diffusion | | |
|-------------------------------------|--------------|--------------|-----------------------|--------------|--------------|
| D_{eff} ($10^{-12}m^2sec^{-1}$) | | | relative to Air | | |
| Bd 1 | 23 °C | 70 °C | Bd 1 | 23 °C | 70 °C |
| CO₂ | 124 | 712 | CO₂ | 33 | 10 |
| air | 3.77 | 71 | air | 1 | 1 |
| cC₅ | 0.128 | 0.418 | cC₅ | 0.034 | 0.006 |
| iC₅ | 0.052 | 0.159 | iC₅ | 0.014 | 0.002 |
| Bd 2 | 23 °C | 70 °C | Bd 2 | 23 °C | 70 °C |
| air | 2.02 | 40.3 | air | 1 | 1 |
| cC₅ | 0.043 | 0.137 | cC₅ | 0.021 | 0.003 |
| iC₅ | 0.018 | 0.073 | iC₅ | 0.009 | 0.002 |

Extracted from Tables 1 and 3 of Ref.⁽⁷⁾

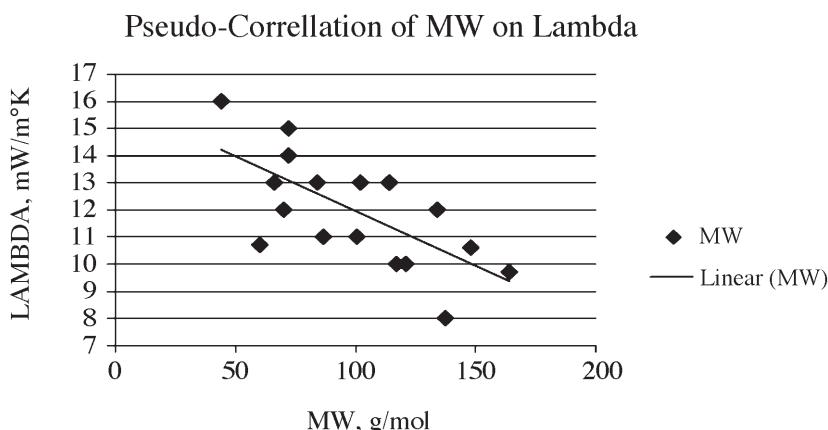


Figure 3. Effect of molecular weight on physical BA's gas lambda values

Table 7. The non-correlation of MW and gas lambda values

| BA | MW [g/mol] | LAMBDA [mW/m °K] |
|-----------|------------|------------------|
| CFC-11 | 137.4 | 8 |
| HFC-245fa | 134 | 12 |
| HCFC-141b | 117 | 10 |
| Ecomate | 60 | 10.7 |

LAB EXPERIMENTS

Foams were made which were blown with HFC-134a, processed through a 30 pound per minute SLUG gun [a low pressure dispensing unit], poured into a 22" tall by 22" diameter [or 4.84 cu ft.] metal cylinder. The resultant foam core, having a density of 1.74 pcf [27.8 kg/m³], was cut into 4 - 8"x8"x2" pieces without skins, to determine the thermal conductivity under various environmental conditions:

- One, aged at 25 °C / 50% RH – labeled RT
- Another aged at 25 °C, in a desiccator – labeled DRY
- A third aged at 25 °C under water – labeled WET, and
- The last, aged at 70 °C / 95% RH – labeled HA [humid aged]

After only 1 week, the DRY specimen had already stopped aging and assumed a flat slope [**Figure 4**], while the RT aged sample continued to climb. This suggests that the water in the air has a strong influence on thermal aging.

The HA sample took off at an even steeper slope, but after two weeks it too had begun to slow its aging rate [**Figure 5**]. Its density also began to climb, from 1.75 pcf to 2.25 pcf [28 to 36 kg/m³] after one week.

Most telling of all was the WET sample, which was aged at room temperature under water – at the end of one week, its density had climbed to 12.6 pcf [202 kg/m³]; a week later to 18.0 pcf [288 kg/m³], and by the third week to 18.9 pcf [302 kg/m³]. The thermal conductivity of this specimen had rocketed to 0.53 BTU-in/(hr)(ft²)(°F) [$\lambda = 76$ mW/m K, **Figure 6**] in only two weeks. This foam had not distorted in any fashion during the immersion.

This rapid change in thermal conductivity strongly suggests that the more water to which you subject foam, the worse you can expect its thermal conductivity to be.

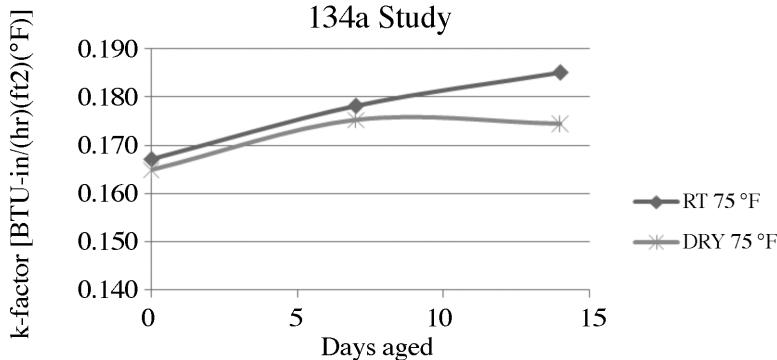


Figure 4. Comparison of same foam exposed to 25 °C, both dry and 50% RH

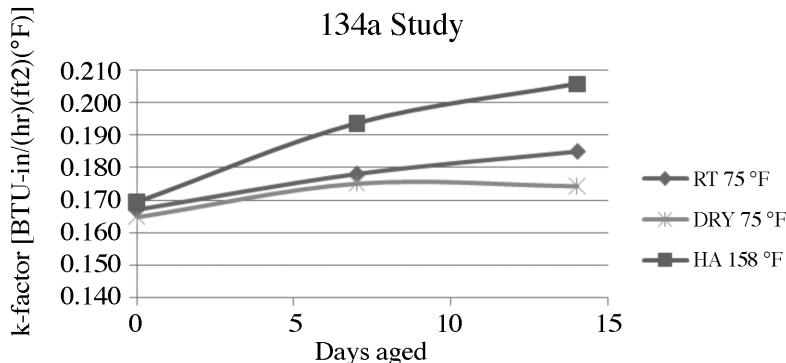


Figure 5. Same foam aged 2 weeks at various conditions – showing magnitude of humid aging

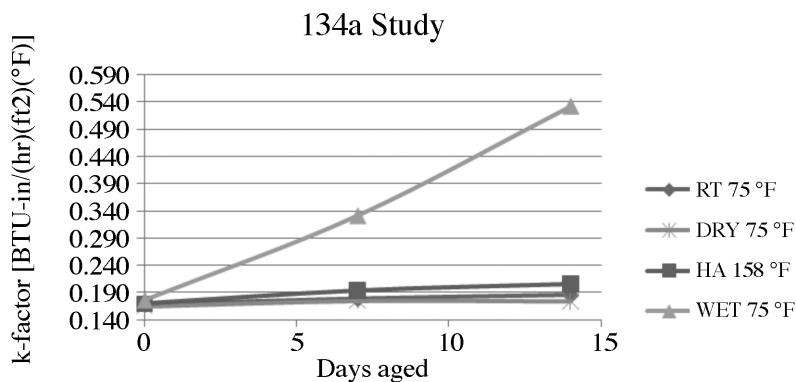


Figure 6. Same foam aged 2 weeks under various conditions – showing magnitude of WET aging

AGED COMMERCIAL UNITS

Since ecomate is the smallest [MW60] physical blowing agent currently on the market, one might expect it to have very poor thermal retention. To demonstrate the long-term permanence of its insulation value, an insulated shipping container, insulated with ecomate® blown pour foam on the 12th of July, 2002 was initially evaluated in the following manner: A block of dry ice was placed into the container and the lid closed and sealed with shipping tape. Ambient temperature was 21 °C. The temperature inside the box was measured with a thermocouple. The test was allowed to stabilize for one hour to reach stasis. The initial temperature was measured and the test recording began from here. The interior temperature was measured and recorded every 24 hours.

5 year retest [Jan 2008] – the box from the original testing was stored in a warehouse for approximately 5½ years. It was re-tested in accordance with the original test method outlined above. The results of that testing are shown in **Figure 7**, which demonstrates that the ecomate blown foam maintained dramatically similar insulation capability that it had 5½ years earlier; it was only one degree C warmer after 72 hours [3 days].

In similar fashion, two identical glass front reach-in refrigerated cabinets insulated with ecomate and HFC-134a respectively, and aged for 5 years, were tested for k-factor change during that period. The k-factor of the ecomate insulated cabinet had changed 4.9% as compared to the HFC-134a cabinet's 12.5% gain [**Figure 8**]. To put that in perspective – a 0.145 initial k-factor

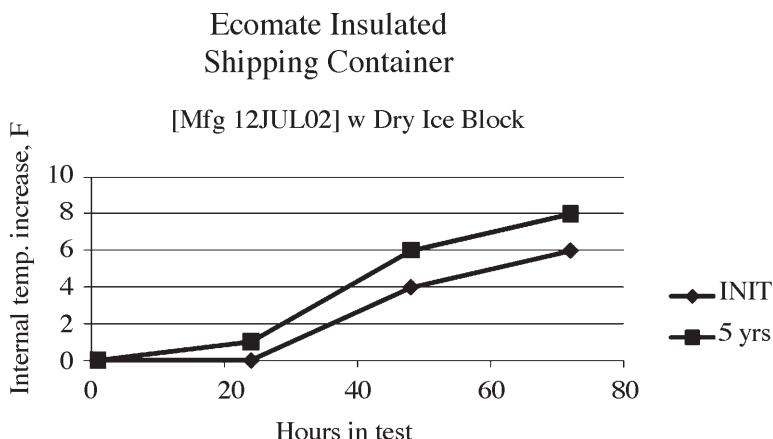


Figure 7. Temperature profiles of re-test of same shipping container aged over 5 years

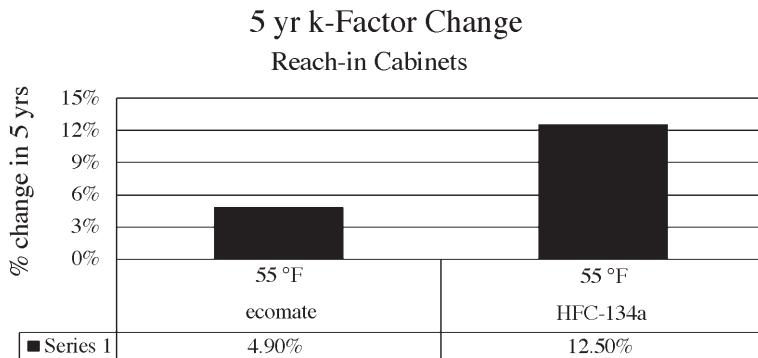


Figure 8. Comparison of the 5 year k-factor stability of ecomate vs. HFC-134a in reach-in refrigerated cabinets

changing to 0.160 would constitute a 10% change during that period. This also demonstrates the excellent thermal retention of ecomate [the smaller molecule].

Many of the products our industry currently builds have foam exposed to the air. That air is laden with moisture. This study demonstrates that moisture will diminish the effectiveness of the foam insulation. If thermal conductivity aging is of paramount importance, we must explore ways to protect polyurethane [PUR] and polyisocyanurate [PIR] foams from atmospheric gas [especially water vapor] intrusion.

CONCLUSIONS

- Literature studies show the marked thermal drift difference with only 50% RH moisture vs. dry foam.
- AHAM studies show that blowing agents DO NOT diffuse out of foamed refrigerators over their lifetime.
- Mathematically - Blowing agent diffusion out of foam is much slower than atmospheric gas [especially water] infusion – at least one third as slow according to Graham's Law [porous foams]; and as much as hundreds of times slower by Fick's Law [non-porous foams].
- Water vapor has horrific effects on thermal conductivity - getting worse with higher water concentrations.

- Even small molecules such as ecomate maintain good thermal resistance over 5+ years if dry.
- Therefore, water vapor seems the predicating factor in k-factor drift.
- Molecular weight is NOT a clear indicator of Thermal Resistance!

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