Ecomate - Environmentally Benign Foam Blowing

John Murphy

Foam Supplies, Inc, Earth City, MO, USA, jmurphy@foamsupplies.com

ABSTRACT

Insulation foams are a critical component in the effort to reduce the amount of energy expended for heating and cooling, thus reducing CO_2 emissions & dependence on foreign oil. A key component of these foams is the captured cell gas, and its insulative capability. These gases [formerly CFCs, HCFCs, and now HFCs] have been shown to contribute heavily to global warming and ozone depletion. Ecomate® is an environmentally sound foam insulation blowing agent. It is non-Ozone Depleting [zero ODP], has little to no Global Warming Potential [GWP], and has such a minimal effect on photochemical smog production that the US-EPA has declared it to be VOC exempt. Ecomate is the only foam blowing agent on the market with these superior credentials. For every 1 MM lbs of ecomate used to replace HFC blowing agent, there is a savings of over 1 MM tons of CO_2 equivalents [GWP].

Keywords: foam blowing agents, global warming, environmentally benign, ecomate

1 INTRODUCTION

In this era of increased awareness of green chemistry, and with rapidly rising fuel costs, the need for superior insulation in domestic and industrial building becomes more urgent & obvious. Superior insulation will diminish the need for heat in the winter and A/C in the summer, thus reducing the dependency on fossil fuels for heating and electrical generation, and reduce our CO_2 emissions.

This paper will outline the several transitions made by the insulation industry to bring the most efficient, most environmentally benign, and at the same time the most cost effective BA to the market. This blowing agent is ecomate®.

The gas inside a foam cell is the agent that keeps the cell from collapsing, and also the agent that keeps heat from transferring from cell to cell. A blowing agent's potential to blow to a given density is proportional to its molecular weight. In other words, the same molar portion of any blowing agent should blow to the same density.

With all its halogen, **CFC-11** [trichlorofluoro-methane] had a molecular weight of 137.7. Foams made with it normally achieved a thermal conductivity [k-factor] of **0.11** BTUin/ft^{2}hrF [or lambda of **15.8** mW/m^{2}K]. The lower the k-factor or λ value, the better the foam insulative performance.

With the transition to **HCFC-141b** [dichlorofluoroethane, MW 117, BP 32ºC], never again did the industry make foams that insulated as well. The new norm became a k – factor of **0.14 [λ=20].**

Then with the transition to **HFC-245fa** [1,1,1,3,3-pentafluoropropane, MW 134, BP 15ºC (a gas at RT)], once again the insulation values declined [**k~ 0.15, λ ~22**]. Not only did thermal properties plummet, but BA prices sky-rocketed. Additionally, special precautions had to be taken to get this BA into the formulations, and to keep it there. Foams blown with **CO_2** [water blown] will do no better than **k= 0.24 [λ= 34.5 mW/m^{2}K].**

Legislation designed to protect the ozone layer has had a counter-productive effect upon CO_2 emissions since currently produced insulation is not as thermally efficient as previously produced with CFC-11. More energy [as heat] will be expended at the previous insulation thickness, or more insulation thickness will be required to preserve the same amount of heat [an economic disincentive]. This is a linear relationship:

Blowing Agent	Optimal k-factor	Thickness for same insulation, in
R-11	0.11	1.0
R141b	~0.14	1.3
R245fa	~0.15	1.4
CO_2	0.24	2.2

Table 1: Impact of BA Change

2 ECOMATE

Ecomate is methyl formate, a material made around the world by many suppliers [and patented for foam blowing by Foam Supplies, Inc. under many active or pending World Patents].

The HFCs [134a, 245fa, and 365mfc] currently being used to blow foams have a huge detrimental impact on global warming, and appear to be persistent in landfills. There is currently strong pressure to eliminate them. If one considers the blowing agent market when all the HFCs have been eliminated from the market, there will be fewer choices remaining: HCs & HFOs. Of these surviving BA candidates, ecomate remains the best choice because it has the best credentials - lowest MW, best solubility, lowest gas lambda, and best environmental properties [Table 2].

	ecomate	n-Pentane	c-Pentane	
PHYSICAL PROPERTIES				
Molecular weight	60.05	72.15	70.1	g/mol
Boiling Point	31.5	37	49	ºC
Liquid density	0.982	0.626	0.751	g/cc
Vapor density	2.07	2.5		g/cc
Gas Lambda	10.7	14	11	mW/mK
Solubility	EXCELLENT	POOR	FAIR-POOR	
FLAMMABILITY				
Flash Point	-19	-40	-37	ºC
LFL	5	1.4	1.1	% v/v
UFL	23	7.8	8.7	% v/v
Heat of Combustion	-16.2	-49.7	-46.9	KJ/g
ENVIRONMENTAL				
GWP	0	11	11	
ODP	0	0	0	
VOC	exempt	YES	YES	

Table 2: Properties of BAs after HFC phase-out

A potential next generation BA class, HFOs [hydro fluoro-olefins], can be readily made from HFC-245fa or HFC-365mfc. These may eventually make it to market, if they pass toxicity testing. While having much improved GWP values, they are still inferior to ecomate. Their price should be as high as the HFCs from which they were derived. That, combined with their high MW, puts them to economic disadvantage. VOC exemption status may also be elusive since olefins have, as a class, very high MIR values. With merely the equivalent lambda values as their predecessors, one must ask ***is it worth the extra cost just to have non-flammability?***

3 ECOMATE - THE BEST CHOICE

- Ecomate **does NOT depend on petrochemicals for its manufacture**. It is made by the carbonilation of methanol [using an alkoxide catalyst]:

$$CH_3OH + CO \rightarrow CH_3OOCH$$

It therefore is not subject to the price fluctuations of petrochemical based BAs as are hydrocarbons.

- It is the **most efficient BA:**
  - Of all BA candidates, it has the **lowest molecular weight** [i.e., it requires less material than the others to produce a given density foam].
  - Ecomate's **boiling point** is lower than the other materials, allowing it to expand earlier in the foaming process.
  - Its **gas Lambda value** is the lowest of the leading candidates – its foams are thermally efficient, equivalent to or better than 134a or 245fa.
  - It has **excellent solubility** for all PU raw materials. Hydrocarbons [such as n-pentane] have to be emulsified in order to be used.

- While flammable, it is the **least flammable** of the leading flammable candidates:
  - Having a **higher Flash Point** than any other candidate;
  - The Lower Flammable Limit is higher by far than the others at 50,000 ppm.
  - Because it is partially oxygenated, its heat of combustion is very low [lower than methanol (sterno)] making any fire both easily contained and easily extinguished.
  - HCs contribute to the burning characteristics of the foams made from them, thus requiring 15-30% additional fire retardant additives usage to obtain the same ratings as previously obtained with HCFCs and HFCs. Ecomate is a drop-in for HFCs in this respect [requiring **NO** additional FRA].
  - Its excellent solubility permits higher flash point systems.

- **Environmentally benign**, ecomate has the best environmental credentials of any material on the market:

  - Its Ozone Depletion Potential is zero.
  - Its Global Warming Potential is negligible.
  - It is VOC exempted by the US-EPA as a photochemical smog producer.
  - It is non-persistent in the environment.

  There is no reason to suspect that its status will change in the future.

4 ATMOSPHERIC CHEMISTRY IMPACT

The Maximum Incremental Reactivity (MIR) Value [the ozone formation potential of a VOC specie and all of its reaction products] for Methyl Formate, per the California Air Resources Board [1], is 0.06 gm O_3/ gm VOC. In Europe, it has a POCP value of 3.

The EPA noted that "methyl formate has no ODP and very low or zero global warming potential (GWP) [2]."
Because of its low MW, less blowing agent is needed per unit density than with other alternatives, there should be substantially fewer emissions using methyl formate.

5 ENVIRONMENTAL PERSISTENCE

Methyl formate rapidly degrades in the environment, usually to give formic acid and methanol. Both of these degradation products are easily transformed by biological agents into water and carbon dioxide [3].

This American Chemistry Council document lists the half-life (at 25°C) of methyl formate in water at 5.1 days at pH 7, and 12.3 hours at pH 8. They further state that methyl formate has a half-life of 5 days in soil. The half-life in air is 1180 hours (about 50 days). It also states that 90-100% of methyl formate is biodegraded after 28 days in activated sludge, with 71% biodegraded in 7 days. Based on these data, methyl formate will not build up in the environment.

6 GLOBAL WARMING IMPACT

BA	MW	NORM	GWP	CO2 e
ecomate	**60**	**1**	**0**	**1**
134a	**102**	**1.70**	**1300**	**2210**
245fa	**134**	**2.23**	**1020**	**2275**
365mfc	**149**	**2.48**	**930**	**2300**

Table 3: CO2 equivalents calculation

For every pound of ecomate used in replacement of HFC blowing agent, there is a savings of over one metric tonne of CO_2 equivalents [GWP]. Replacing an HFC having a GWP value of ~1000 with a ZERO GWP product, in addition to having a MW less than half that of the HFC it replaces [i.e., half as much needed to achieve equivalent density], allows ecomate to accomplish this. And since ecomate does not contribute to photochemical smog, it can be used in Air Pollution Containment Districts without disrupting the environment, nor displacing jobs.

The United Nations Environmental Protection Agency is conducting several Developmental Programs around the world verifying the merits of ecomate in urethane foams, and to assist developing regions of our planet to convert from HCFCs and HFCs all the more rapidly.

Using ecomate, a leading manufacturer of custom refrigeration equipment has surpassed Energy Star standards by an average of 23.7% on its products receiving the Energy Star award.

Foams made with ecomate have shown equivalent performance under actual use conditions to foams made with 134a and 245fa despite its lower molecular weight. We believe this to be so because ecomate makes very fine, micro-cellular foams exhibiting excellent flow ability [to better fill parts] & with equivalent physical properties to foams made from other BAs.

Using ecomate instead of HFCs will dramatically reduce the long term emission of Greenhouse Gases from polyurethane insulating foams without additional environmental impact. Ecomate offers equivalent insulation, superior environmental properties, and at a much lower cost. **Its time has come!**

REFERENCES

[1] California Air Resources Board "ARB Aerosol Coating Regulation" http://www.arb.ca.gov/coatings/arch/reactivity/draft_react_app_a.pdf

[2] 40CFR Part 65, Volume 65, Number 243, 78977-78989. http://www.epa.gov/Ozone/snap/regs/65fr78977.pdf

[3] American Chemistry Council document on formic acid and formates, Parts 1-5 p5-8. http://www.epa.gov/hpv/pubs/summaries/formates/c13438.pdf