<u>Ecomate – Environmentally Benign Foam Blowing</u> – Abstract

Ecomate® [methyl formate] is an environmentally sound alternative 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 USEPA has declared it to be VOC exempt. Ecomate is the only foam blowing agent on the market with these superior credentials.

For every pound of ecomate used in replacement of HFC blowing agent, there is a savings of over one metric ton of CO_2 equivalents [GWP]. 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.

While the transition from CFCs, to HCFCs, to HFCs has meant compromised thermal efficiencies in the foams produced by each succeeding transition, it has been shown that ecomate can produce foams with equivalent thermal properties to those obtained with current HFCs. And since ecomate requires only half as much material to achieve an equivalent density, it becomes even more environmentally benign, not to mention more cost effective. Using ecomate instead of HFCs will dramatically reduce the long term emission of Greenhouse Gases from polyurethane insulating foams without additional environmental impact.

<u>Ecomate – Environmentally Benign Foam Blowing Agent</u>

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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.

While there are many insulation materials on the market today, a superior product should minimize drafts, as well as reduce convective, conductive, and radiant heat losses. Most fibrous products, such as fiberglass or cellulose fibers [albeit inexpensive] rely on their ability to trap dry air. Their weaknesses lie in the fact that they can settle, and they do not protect well against air infiltration [especially moist air]. And since they rely on dry air as the insulative media, they can easily be bettered by products having captive non-conductive gases superior to dry air. These products are foams.

Foams come in many varieties. For insulation purposes the polymers are essentially polystyrene and polyurethane based, with some phenolic resin still used. The effectiveness of these products depends heavily upon how well they capture and retain their non-conductive gases [or blowing agents], upon the nature of the blowing agents themselves, in addition to how well they are applied.

So what makes a good foam blowing agent? More importantly, why do we use the materials we use today? 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®.

A good blowing agent for foams has many attributes:

- It does not react with any of the raw materials
- It solubilizes all the raw materials used to produce the foam,
- It does not dissolve the final foam,
- It has a boiling point just slightly above room temperature [it is a Liquid], and
- It affords the finished foam good thermal properties.

In the past there was one other important criteria, non-flammability! But with the restrictions place on BAs containing any halogen [because of their high ozone depletion potential, ODP], they can no longer be used. So that, in a nut-shell, leaves in our future only flammable liquids [or gases, either flammable or atmospheric].

A bit on the history of BAs in foam is warranted at this point. Initially water and a few organic solvents [such as acetone and methylene chloride] were attempted. Water [BP 100C] works by reacting with the isocyanate to form CO_2 and an amide [which further reacts with the isocyanate]. For rigid foams [which have predominately closed cells], CO_2 blowing was acceptable, but the use of acetone [BP 56C] or $MeCl_2$ [BP 42C] caused foam collapse because the solvency of these materials was too strong for the finished foams. Additionally, acetone was flammable.

With the advent of CFCs, the rigid market found the tool it needed to really 'expand' as an insulation. CFC-11 [trichlorofluoromethane] became the blowing agent of choice because it had all the aforementioned attributes: it dissolved the raw materials w/o reacting with them, it did not dissolve the foam, its boiling point was 23.7 ºC, it was non-flammable, and it afforded excellent insulation.

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. The larger the molecule, generally the better insulative effect it might have [all other factors held equal]. It is much harder to push a boulder than a grain of sand.

With all its halogen, **CFC-11** had a molecular weight of 137.7, and was a figurative boulder inside each cell. The foams made with it normally achieved a thermal conductivity [k-factor] of **0.11** BTUin/ft^2hrF [or lambda of **15.8** mW/m^2K]. The lower the k-factor or λ value, the better the foam insulative performance.

Foams blown with **CO_2** [water blown] will do no better than **k= 0.24 [λ= 34.5 mW/m^2K].** Other atmospheric gases will do no better. And moisture makes them much worse. The same is true of fibrous materials, although they have the additional disadvantage of being open [drafts can pass easily through them and mitigate any insulative effect], and prone to settling.

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].**

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.

Thus it becomes clear that legislation designed to protect the ozone layer has had a counterproductive 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 same 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:

Table 1	Optimal k-factor	Thickness for same insulation, in
R-11	0.11	1.0
R141b	0.14	1.3
R245fa	0.155	1.4
CO_2	0.24	2.2

So what is ecomate, and how does it compare to current BA candidates?

Chemically, 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]. If one considers the blowing agent market when all the HFCs have been eliminated from the market, there will be few choices remaining. Naturally ALL candidates will then be flammable, since they will have no halogen content.

Of these surviving BA candidates, ecomate remains the best choice because it has the best credentials [Table 2].

Table 2: Properties of BAs after HFC phase-out

	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	

Why is ecomate the best choice?

- First of all ecomate **does <u>NOT</u> depend on petrochemicals for its manufacture**. It is made by the carbonilation of methanol [using an alkoxide catalyst]:

$$\mathbf{CH_3OH + CO \rightarrow CH_3OOCH}$$

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

- It is the **<u>most efficient</u> BA:**
  - Of the leading non-halogenated candidates, it has the lowest molecular weight [which means it requires less material than the others to produce a given density foam].
  - While still a liquid, its boiling point is lower than the other materials allowing it to get started earlier in the foaming process.
  - Its gas Lambda value is the lowest of the leading candidates – it produces foams with the lowest thermal conductivities, ie, they are the most thermally efficient.
  - It produces foams with efficiencies equivalent to 134a or 245fa.
  - It has excellent solubility for all the raw materials currently used in polyurethane manufacture. Hydrocarbons have to be emulsified in order to be used.

- While flammable, it is the **<u>least flammable</u>** of the leading candidates:
  - Its Flash Point is higher than any other candidate;
  - Its LFL [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].

- **<u>Environmentally benign</u>**, ecomate has the best environmental credentials of any material on the market:
  - Its Ozone Depletion potential is zero.
  - Its Global Warming Potential is 'little to none'.
  - It is exempted by the USEPA as a photochemical smog producer, or VOC.
  - It is non-persistent in the environment.
  - There is no reason to suspect that its status will change in the future.

Atmospheric chemistry impact

The Maximum Incremental Reactivity (MIR) Value [the ozone formation potential of a VOC specie and all of its reaction products], per the California Air Resources Board [1], is 0.06 gm O_3/ gm VOC. Other compounds which have received VOC Exempt in the State of California have MIR values greater than 0.06. Below is a list of several VOC Exempt compounds along with methyl formate:

Compound	Maximum Incremental Reactivity (MIR) Value
Methyl Formate	0.06
Methyl Acetate	0.07
Ethane	0.31
Acetone	0.43

Ozone formation

Tropospheric ozone formation will not be impacted by the use of methyl formate as a blowing agent for foams. Ecomate's very low MIR of 0.06, plus the encapsulation of the blowing agent as part of the foam process will lead to no impact on ozone levels. In fact, if methyl formate is used to replace pentane, there will actually be a reduction in the amount of ozone produced. Because less blowing agent is needed per unit density than with other alternatives, there should be substantially fewer emissions using methyl formate.

Stratospheric Ozone Depletion

The EPA noted that "methyl formate has no ODP and very low or zero global warming potential (GWP)[2]." p78980). In short, methyl formate will be replacing some use of HCFC-22, which has an ODP of 0.05. For polystyrene foam, methyl formate will be replacing HCFC-142b which has an ODP of 0.065. Therefore, the replacement with methyl formate will have a positive impact on the depletion of ozone in the stratosphere. Other alternative blowing agents also have zero ODP.

Climate Change

Methyl formate is designed to replace HCFCs and HFCs. HCFCs have measurable ODP. HCFCs and HFCs are GWP compounds. The EPA noted that "methyl formate has no ODP and very low or zero global warming potential (GWP).[3]" The GWP data are summarized in the following table.

Blowing Agent	Global Warming Potential (GWP)
Methyl Formate (ecomate®)	<1.5
HCFC-22	1700
HCFC-142b	2400
HFC-134a	1300
HFC-245fa	950
n-pentane	11

Table 3: "Greenhouse Gases and Global Warming Potential Values[4]"

Based on these data, using methyl formate to replace any of the above listed blowing agents would reduce the amount of global warming compounds emitted to the air.

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[5].

This American Chemical 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.

For every ton of ecomate used in replacement of HFC blowing agent, there is a savings of over 2000 tons 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.

Use in foams

Ecomate has been commercialized in **rigid urethane foams** for over 10 years. It is being used in pour-in-place & spray formulations with great success. 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.

To examine efficiencies of ecomate in foams v HFCs we examined not only the thermal conductivities of the foams produced but also those foams used in actual full scale side-by-side applications. The best evaluations are ALWAYS run side-by-side, using commercial cabinets run under actual use conditions, in which one measures either energy used, ice melt over time, compressor cycles, or temperature change with time, for example.

In our first example, two identical foam insulated drink dispensers [one foamed with 134a, the other with ecomate-blown foam] were compared by monitoring the amount of ice melt over time when utilized at 75ºF ambient.   Figure 1 shows the identical results obtained using either foam BA.

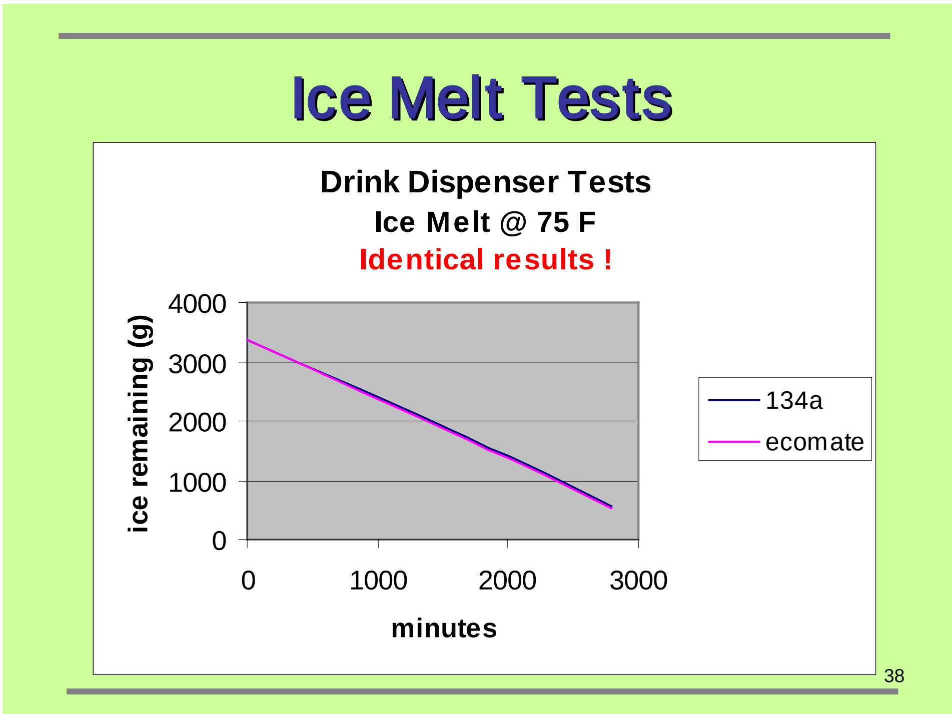

Figure 1: Identical results with 134a, ecomate blown foams

In a second example, two identical, foam insulated vendor display cabinets [one insulated with HCFC-245fa blown foam, the other with ecomate] each having a 40º F chiller were fitted with five 100W light bulbs on the bottom of its cabinet. The duty cycles [time on] of each cabinet to maintain 95 ºF within the cabinet were monitored. The cabinet insulated with 245fa blown foam was on for 36.8% of the time; the ecomate cabinet for 37.4%. These nearly identical results suggest that ecomate can be substituted as a foam BA for either 245fa or 134a with no loss in insulating efficiency.

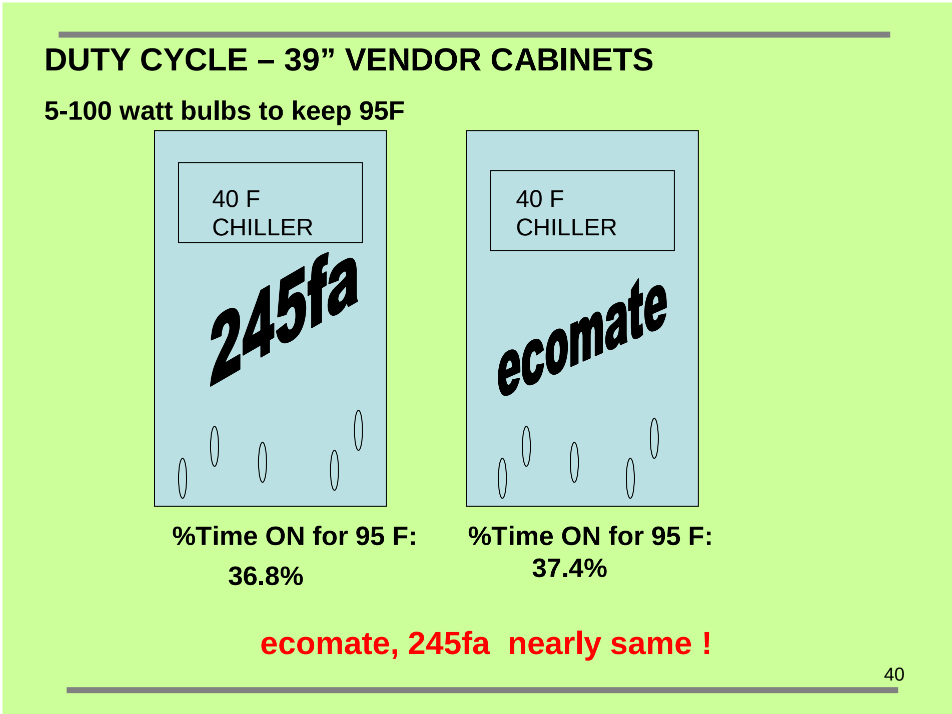

Figure 2: Comparison of 245fa, ecomate foamed vendor cabinets

ECOMATE IN OTHER FOAMS

It has recently been successfully trialed and commercialized to blow **flexible slabstock** foam. In these type foams, the cells normally open and all the BA is immediately lost to the environment. It works equally as well with MDI or TDI based foams, giving MDI foams the same handling characteristics as with the more volatile TDI. The use of ecomate in these types of foams will allow for the use of a safer isocyanate, and reduce environmental impact and save jobs in certain containment areas of the country.

Ecomate is also the best substitute for 141b in **self skinning elastomers**. It has almost identical boiling point and solubility characteristics to 141b. What this means is that it will produce foams with strong skins and low core density in the same fashion as those produced with 141b. Other materials carry greater flammability risk, potentially thinner skins, lack of density latitude, or all of these.

Ecomate cannot do everything! It does not have the vapor pressure of gases used to produce froth foams. These foams were useful when foaming against cold substrates, having difficult mold configurations to fill, or having loose fitting molds [the higher apparent viscosity of a froth prevented leakage]. Ecomate is being trialed in PS and poly-olefinic foams. The high solubility of ecomate may make success in these areas elusive.

However, using ecomate instead of HFCs will dramatically reduce the long term emission of Greenhouse Gases from polyurethane insulating foams without additional environmental impact.

[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] 40CFR Part 65, Volume 65, Number 243, 78980.
http://www.epa.gov/Ozone/snap/regs/65fr78977.pdf

[4] "Greenhouse Gases and Global Warming Potential Values," US EPA, April 2002.
http://www.epa.gov/climatechange/emissions/downloads/ghg_gwp.pdf

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