Ecomate in Flexible Slabstock Foams, Part II

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ABSTRACT:

Last year we introduced ecomate to the flexible slabstock industry. At that point we had no full scale commercial runs. With two under our belts at the time of this writing, we would like to share these success stories demonstrating the safety and low cost of conversion, the ease of use, and the properties obtained. Ecomate produces foams similar to those blown with acetone or methylene chloride, but with a lower boiling point [more efficient]. Ecomate is a safer alternative to acetone. Because of its excellent solubility, ecomate gives slightly softer foams than those formerly achieved with HCFC-141b. It produces very low density foams with very good hand.

Ecomate is vastly superior to water, which builds polyurea giving a boardy feel to foams, and which is poorly compatible with many urethane raw materials. Hydrocarbons suffer from extremely poor solubility, from high flammability, and have VOC issues. Because of these deficiencies, neither is considered as a blowing agent for flexible slabstock

An ideal combination of boiling point and solubility mimicking the solubility and boiling point of 141b makes ecomate an ideal blowing agent in slabstock foams. No special equipment is needed to dispense it. With about half the molecular weight of 141b and very similar to that of acetone, it compares very favorably to acetone as a foam blowing agent. Because of its lower boiling point it could save on catalyst costs. Combining this efficiency and economy of use with the environmentally friendly nature of ecomate [zero ODP, zero GWP, and VOC-exempt] there is no doubt that it can be highly appealing to this market.

ECOMATE

As reported earlier[i], ecomate is a patented blowing agent[ii] for polyurethane foams that has many of the most desirable attributes that one seeks in a blowing agent [Table 1]:

Table 1	ecomate	141b	HFC 245fa	HFC 365mfc	n-pentane	Cyclo-pentane
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

Ecomate is also a non-GWP [Global Warming Potential], non-ODP [Ozone Depletion Potential] blowing agent which is also VOC [Volatile Organic Compound] exempt. It exhibits excellent solubility in all urethane components, which allows the formulator the opportunity to use more desirable polyols for improved physical properties – such as flammability, dimensional stability, and compressive strength. One obtains all this while using less surfactant, lower amounts of fire retardant, and at lower isocyanate indices. One also achieves better economies because of ecomate's low molecular weight, and the fact that it is not a hydrocarbon lends stability to its pricing.

Ecomate is useful in many different types of foam. Its use in rigid foams, especially in isocyanurate boardstock and pour-in-place foams has been extensive covered previously[iii,iv,v]. It can be used not only in rigid foams, but also in integral skinned elastomers, and flexible foams as well.

INTEGRAL SKINNED FOAMS

The ideal combination of boiling point and solubility to mimic the solubility and boiling point of 141b makes ecomate the ideal replacement for HCFC 141b in integral skin foams. With about half the molecular weight of 141b, it is all the more economical for this application. Combining this efficiency and economy of use with the environmentally friendly nature of ecomate [zero ODP, zero GWP, and VOC-exempt] there is no doubt that it is highly appealing to this market.

Table 2: Cost Efficiency of New BA Materials

BLOW. AGENT	$/lb	MOL WT	FACTOR	$/MOLE
HCFC-141b	▲▲	117	1.00	REF
HCFC-22	▲▲	86.5	0.74	- 25 %
HFC-245fa	▲▲▲▲	134	1.15	+ 350 %
HFC-365mfc	▲▲▲▲	148	1.26	+ 380 %
Ecomate	▲	60	0.51	**- 65 %**
cC5	▲▲	70	0.60	- 45 %
nC5	▲	72	0.62	- 70 %

For instance:

Since many integral skinned foam formulations contain pigmentation which greatly increases viscosity, the formulator will find that ecomate will lessen those viscosity concerns because ecomate has excellent solubility for all urethane raw materials resulting in markedly reduced system viscosities.

Because of this solubility, ecomate will also give slightly softer foams than those formerly achieved with HCFC-141b. Ecomate can then reduce or eliminate the need to use non-reactive plasticizers which have a tendency to slowly exude out and cause glass fogging in automobile applications.

Ecomate blown integral skinned foams give excellent skin formation even at elevated mold temperatures [i.e., 30-35 °C (or 85-95 °F)] which allows earlier de-molding of parts, which equals greater efficiency of operation.

With the high cost of blowing agents these days, ecomate offers the best alternative to 141b from an economical stance [see Table 2]. In addition, it forms much stronger skins at equivalent mold temperatures than HFC 245fa because of its enhanced solubility and lower boiling point.

It is vastly superior to water, which generates CO2 [tending to minimize skin thickness] and builds polyurea, which gives a boardy feel to foams blown with it, and is poorly compatible with many urethane raw materials. Hydrocarbons have also been attempted as blowing agents but they also suffer from extremely poor solubility, and from high flammability.

While ecomate itself is flammable, when blended into the polyol matrix at less than 6 wt %, that polyol blend generally does not have to be placarded with a red "Flammable" label, and can be used safely in most plant environments already ventilated sufficiently to use isocyanates.

What makes it unique in integral skinned foams is a combination of: 1) its ability to solvate all of the polyester and polyether polyols currently in use with HCFC-141b blown elastomers; 2) its perfectly suited boiling point, just above ambient [similar to 141b], which allows good skin formation without expensive cooling, 3) its benign effect of the environment [non-GWP, non-ODP, and VOC exempt] and 4) its low molecular weight. The fact that it has half the molecular weight of 141b, therefore requiring half its weight for equivalent density, and that it is very economically situated make it very appealing to this segment of the industry. Needless to say, patents are pending for this application.

In addition ecomate has **SNAP** approval for use in integral skin polyurethanes as an alternate to CFCs and HCFCs from the US EPA. While HFC 245fa has similar approval, it has much poorer solubility, a sub-ambient boiling point, higher molecular weight and higher cost than ecomate. At the time of this writing, neither HFC 365mfc nor the HFC 365mfc/227ea blends have been approved for integral skinned foams. Even if they were to gain such approval, they are not available for use in North America, and their MW & costs may well make them economically prohibitive.

FLEXIBLE SLABSOCK FOAM

In the United States today, slabstock foams are blown with either Liquid CO2 or acetone. This blowing agent is entirely lost to the atmosphere when the foam cells are opened. So there is considerable loss of blowing agent into the atmosphere in the manufacture of this type of foam.

The majority of foamers are using liquid CO2, while only a small handful use acetone as their BA. We believe that ecomate could be a safer alternative blowing agent to acetone. The effects of long-term exposure to acetone are known, mostly thru animal studies. Kidney, liver, and nerve damage, increased birth defects, and lowered reproduction ability of males [only] occurred in long term exposure of animals to acetone.

Table 3 shows that while ecomate and acetone have nearly the same molecular weight [important for identical loadings to give the same density], the boiling point of ecomate is much lower which would allow faster foaming with less catalyst [an economic advantage]. But why is ecomate safer than acetone?

Table 3: Physical Properties	**Ecomate**	Acetone
Mol Wt	60	58
B Pt, °C	32.1	56.3
LEL, vol%	5	2.5
UEL, vol%	23	12.8
Heat of Vaporization, BTU/Lb	202.3	234
PEL, ppm	5000	1000
TLV, ppm	100	500

For one, while both materials are flammable, the lower explosive limit of ecomate is TWICE that of acetone. **It is less apt to reach LEL,** especially at foam blow-off! The Permissible Exposure Limit is FIVE times greater that of acetone, which means that the worker can be exposed to 5 times the concentrations of acetone without adverse effects. **It is less hazardous to use!** In addition, the Threshold Limit Value [the lowest amount the average person can detect] is five times less than acetone. **It is easier to detect!**

Both materials are VOC exempt. Both materials are non-Ozone Depletors. And while both materials have negligible Global Warming Potential, ecomate GWP values are lower than those of acetone. **It is more benign to the atmosphere!** Ecomate is less solubilizing to the oils in the skin and is less likely to cause dermatitis than is acetone.

The toxicity of formate materials has been extensively studied by the EPA. In a report by Dr Rauchman [vi] to the US EPA concerning the toxicity of ecomate [methyl formate], he states:

- The **acute toxicity** of all Formate materials is **low** with no special hazards
- **Methyl Formate [MF] is transformed very rapidly into formic acid and methanol in the body**
    - **with a half-life on the order of several seconds.**
- **Formic acid** is **present in many foods** (18)
    - e.g., fruits (20 -40 ppm),
    - fruit juices (30 -100 ppm),
    - fruit syrups (650 -1630 ppm),
    - honey (20 -2000 ppm),
    - wines (1 -340 ppm),
    - coffee, roasted (1350 -2200 ppm),
    - coffee, extracts (2000 -7700 ppm),
    - evaporated milk (30 -400 ppm), and
    - cheese (20 -200 ppm) (19). (20). (page 14)
- The 4-hour **inhalation LC50** of methyl formate was **> 21 mg/L**
- All found **negative** in the **Ames test**
- No further testing is recommended

Thus it can be assumed that ecomate presents no toxicological burden.

Molded flexible foams made with ecomate are comparable to those made with other physical blowing agents. We expect the same with slabstock foam. When used in rigid foam, there was a benefit to using ecomate in lieu of hydrocarbon BAs- less fire retardant agent was necessary to achieve desired fire properties. This may also be true in slabstock foam.

SLABSTOCK TRIALS

We ran two trials in the recent past which ran so seamlessly that we want to share some aspects of each with you.

We will use the first trial as an example of our pre-trial methodology to assure safe handling and use of ecomate: this involves visitation, consultation, calculation, set-up and inspection. We visit the prospective user and examine his current set-up. In particular we want to see how they currently are handling their BA, and to determine what amount of exhaust they had on their foam line. We then consult with them on ways to store, transfer, and use ecomate safely without significant equipment changes or expense. Our engineers work with their production and engineering personnel directly. And we worked with the local fire Marshal to get the set-up approved.

As a part of the consultation are calculations of total ecomate usage anticipated, loss factors and percentage of LEL that might be obtained with the lowest density foams formulated. It might normally be assumed that if they have sufficient exhaust on the line to handle TDI safely that they can safely handle ecomate. We calculate the amount of ecomate required, and the amount of ecomate effusion from their lowest density formulations [highest BA loadings] to verify that the LEL is not approached.

The first trial involved the change-over from a halocarbon blowing agent to ecomate. The customer said that their lowest density foam required 27 lbs/min of BA to produce, and that their line had 4 - 16,000cfm exhaust fans that in total removed 64,000 cfm of gases.

Calculation of percent of LEL generated

- First, assume that the values are right:
  - Formula emits a max of 27 lbs / min ecomate Blowing agent = 12,258 g /min
  - The tunnel exchanges at the rate of 64,000 scfm [= 4*16000cfm].

- Next, we assume that this represents the volume we are calculating - 64,000 cu.ft.
- And the concentration we will have, 12,258 grams

- We calculate the volume in liters: 64,000 * 28.317 liter/cu ft = **1,812,278 liters** [We assume that it is AIR for maximum O_2 content]

- Then we calculate the concentration of ecomate:

  - 12,258 g / 60.05 g/mol = 219.25 moles
  - 1 mol of gas = 22.4 liters
  - 219.25 moles * 22.4 liters/mol = **4911.24 liters of ecomate**

- Finally, since the LEL [Lower Explosion Limit] is given in a vol% of gas in a vol% of air:
  - 4911.2 liters ecomate / 1,812,278 liters of Air = **0.27 vol% ecomate**
- **This is far below the LEL of ecomate = 5.0 vol %**

Thus we are assumed that this concentration might be safely handled by this equipment if everything is fully operational. The ecomate connections were engineered, using existing equipment, so that the BA was stored outside, and N_2 pressure driven to the transfer pump inside of the plant.

The ecomate was transferred to the mix line via N_2 pressure, to a transfer pump and flow meter, and then into the polyol manifold. Ecomate has such good solubility in all raw materials that a simple static mixer was all that was required for total mix.

It was determined that in the trial we would run two separate formulations which represented the lowest density and highest throughput systems that they had, to determine if there might be any problems with emissions, or with the physical properties of the foams made with ecomate.

The two systems were their 'X' grade [coded here for confidentiality], run for 5.5 minutes at a 22 lb/min BA usage, and then transitioning to a system nearly as low in density but with a lower throughput, 'Y' grade, run at 9.5 lbs /min for an equal amount of time. It was decided that the highest amount of off-gassing would occur at those points of highest foam disturbance: at the foaming trough, the blow-off point [cell opening], at the removal of side sheets, and at the cut-off saw. In addition, we monitored beneath the line at the trough. The emissions monitoring results are in Tables 4 & 5:

Table 4: Ecomate Monitoring for System X			
Position	Meter Reading (% of LEL)	Baseline Reading (% of LEL)	Actual Level (% of LEL)
Trough	4%	2%	**2%**
Blow-off point	3%	2%	**1%**
Side skin removal	3%	2%	**1%**
Under line	2%	2%	**0%**
Cut-off saw	4%	2%	**2%**
End of run	Not Measured	2%	-
Throughput of foam	433.9 lbs/min		
Ecomate Throughput	22 lbs/min (4.8% of system)		
Duration of formula	5.8 min		
Pounds of foam	2516.7 lbs		

Table 5: Ecomate Monitoring for System Y			
Position	Meter Reading	Baseline Reading	Actual Level
Trough	3%	2%	**1%**
Blow-off point	3%	2%	**1%**
Side skin removal	2%	2%	**0%**
Under line	2%	2%	**0%**
Cut-off saw	Not Measured	2%	-
End of run	2%	2%	**0%**
Throughput of foam	466.58 lbs/min		
Ecomate Throughput	9.5 lbs/min (2.00% of system)		
Duration of formula	5.3 min		
Pounds of foam	2472.9 lbs		

The LEL for ecomate is 5 vol%, or 50,000 ppm. Two pct of the LEL is a mere 1000 ppm, a very low value and verifies our previous calculations about the safety of the operation. The foams produced were in every way equivalent to those produced by their former BA. The formulas used approximately 25% less ecomate than with the previous BA, and produced comparable densities [**0.89 & 0.96 pcf,** respectively]. Both parties involved deemed these runs a success!

Another customer has used ecomate to make slabstock and visco-elastic foams from MDI. He reports that the foams are as soft or softer than their TDI cousins, and less toxic to produce. With ecomate he can reach all density ranges of his former TDI formulations. He is paying less for ecomate than his previous BA, and he is using a lesser quantity. He is quite satisfied with his conversion.

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1 API POLYURETHANES 2005 Technical Conference, *ecomate® Foam Blowing Agent*, John Murphy, Mark Schulte, Buck Green, 10/18/2005, pg. 302ff

ii US 6,753,357, others pending.

iii Ref 1

4 Utech 2006, *Ecomate -The Revolutionary New Blowing Agent for Europe*, John Murphy – Foam Supplies, Inc & Dennis Jones, BOC Ltd. Paper #18, March 28, 2006

5 Rappra06, *Ecomate – A Revolutionary yet Economical New Blowing Agent*, John Murphy – Foam Supplies, Inc; Dennis Jones, BOC Ltd. , Munich, 5/16/2006

vi U.S.EPA HPV Chemical Challenge Program, Revised Test Plan for the Formates Category, Dr Elmer Rauchman, PhD, DABT Toxicology and Regulatory Affairs, May 27, 2003

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.