

Ecomate in Flexible Slabstock Foams
John Murphy
Foam Supplies, Inc

ABSTRACT:

Ecomate produces foams similar to those blown with acetone, 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 earlierⁱ, ecomate is a patented blowing agentⁱⁱ for polyurethane foams that has many of the most desirable attributes that one seeks in a blowing agent [Table 1]:

| <u>Table 1</u> | <u>ecomate</u> | <u>141b</u> | <u>HFC</u> <u>245fa</u> | <u>HFC</u> <u>365mfc</u> | <u>n-</u> <u>pentane</u> | <u>Cyclo-</u> <u>pentane</u> |
|--------------------|----------------|-------------|----------------------------|-----------------------------|-----------------------------|---------------------------------|
| 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 twice as safe to handle!** 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 safer 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.**
- **MF 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.

While we have run ecomate in molded slab, we have not used it on a full continuous line at the time of this writing. We are confident that it will perform very well, and we are in negotiations to run such a trial. The combination of lower boiling point [which should lead to lower catalyst consumption], low toxicity and increased handling safety, ought to be sufficient inducement to: Try us, you'll like us!

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.