ecomate® - a multi-faceted Blowing Agent

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ABSTRACT

Since its introduction into the foam market as a new blowing agent, ecomate® has been successfully trialed in many different venues. We will outline below difficult applications that have been successfully met using ecomate.

Ecomate seems the ideal replacement for HCFC 141b in integral skin foams because ecomate has the ideal combination of boiling point and solubility to mimic the solubility and boiling point of 141b. Additionally it has about half the molecular weight of 141b making it even 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.

Another market having a difficult transition from 141b has been the spray foam market. The use of HFC 245fa is fraught with problems because of high drum vapor pressures causing ratio issues in the field. HFC 365mfc [while not available in North America] would have better drum pressures, but has difficulty with cold substrates; and has such a high MW as to be less than economical. HC's are problematic because of solubility and flammability issues, and are losing some of their cost advantage due to recent price increases. We will show how ecomate can help mitigate the application problems of spray foam blowing agent transition both neat and in combination with other physical BAs.

Finally we will show how ecomate can be used in pour foams to make economical foams having good dimensional stability, with excellent flammability, at low densities.

ECOMATE

As reported earlier[1], ecomate is a patented blowing agent[2] 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[3,4,5]. 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.

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.

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 %

SPRAY FOAM

Spray foams are exactly like other rigid foams with three exceptions: they are much faster reacting, they must have prolonged shelf stability, and they are almost always applied at 1:1 by volume. Almost all spray foam used today also has to be Class II [75 flame spread & < 450 smoke] or better.

To achieve the requisite faster spray reactivity one can increase the amount of amine and metal catalysts, but this is generally a costly approach and is not usually suited to longevity on the shelf. The other approach is to incorporate a certain amount of reactive polyols – such as tertiary amine based or mannich based polyols which afford much longer shelf stability. One of the down sides of this approach is that amine based polyols tend to increase the amount of smoke generated in fire tests.

To improve fire properties [flame spread and smoke] and reduce formulation costs, many formulators are using an increasing amount of polyester polyols in their formulations. These polyols bring a high amount of aromaticity into the formulation, which naturally improves burn resistance. Since these polyols are approximately 2 functional, an increase in formulation index is mandated to obtain good foam physical properties which pushes up formulation cost. Another detriment to using polyester polyols is their very poor solubility characteristics – a factor very easily overcome with the use of ecomate as the foam blowing agent.

Now all we have to do is to put all this in a package at 1:1 by volume and maintain a reasonable index. An effective spray foam formulation usually requires a combination of polyols to bring all the properties required of it – fast reactivity and prolonged can stability requires some reactive amine polyol; for strength, a certain amount of sucrose polyol; for fire resistance, a certain amount of high aromatic polyester; and for good flow and adhesion, a quantity of mannich base polyol. But what might be the best ratio of ester to mannich to amine to sucrose polyols? This seems an ideal situation for an experimental design mixture solution!

So we trialed the following resins in a formulation containing 15 parts FRA per 100 polyol and 2.5% water and 6% ecomate to achieve a 2 pcf IPD spray foam:

Table 3: The Design	Range
DMT ester [EqWt = 184]	(20 to 50 parts)
Mannich [EqWt = 178]	(20 - 40 parts)
Sucrose [EqWt = 152]	(0 - 30 parts)
Amine [EqWt = 94]	(0 – 25 parts)

We looked for the effects the polyol mixtures had on index at a 1:1 volume ratio, as well as on flame spread and smoke. The design is shown in Table 3. The design consisted of a d-optimal mixture factorial design of twenty foam formulations, designed and analyzed using Design-Expert® 6.0 software. The indexes of these foams when run at 1:1 by volume ranged from 104 to 119, which is not unusual for spray foams.

The formulations were compounded and tested for fire resistance using a modified Monsanto Tunnel which allows us to monitor the flame spread and smoke generated in the burning of these foams. We wish to add the caveat that the burning characteristics of foams obtained in small scale tests may not be indicative of what happens in full scale conflagrations. We have seen very good correlation between our tunnel and the full scale Steiner Tunnel in both Flame Spread [FS] and Smoke values. The results are shown in Figures 1& 2. The interpretation of these graphs is quite simple. In Figure 1, the amine level is held constant at 12.5%, the other three ingredients are varied within the experimental range [sucrose 0-30%, ester 20-50%, and mannich 20-40%] from each base [low value] of the triangle to the apex opposite. The response, Flame Spread, increases from just under 35 to just over 55, and is almost directly related [parallel] to sucrose concentration in the mixture.

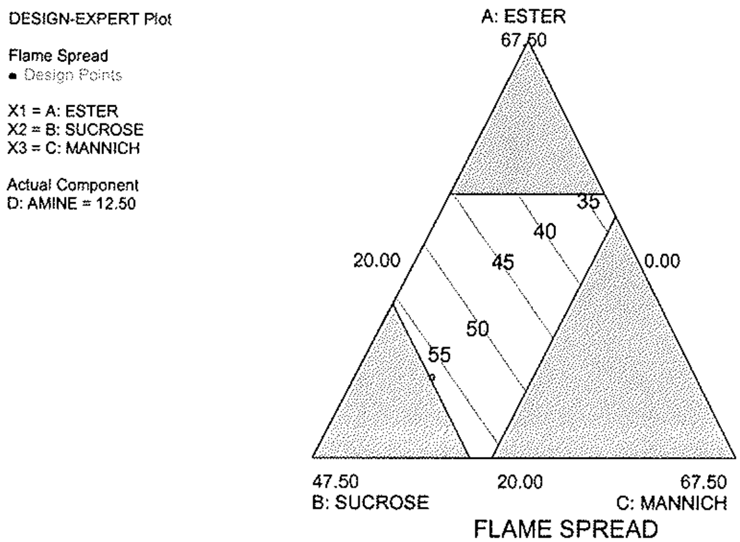

Figure 1: Flame Spread

Amazing here was that this information disputes a long held philosophy that sucrose polyols were good for flame spread because they helped to develop good char. One can see from Fig. 1 that flame spread becomes progressively worse with increasing sucrose levels.

What about smoke levels?

In Figure 2, the amine polyol concentration is held at zero. The ester base level is 20% to a high of 80%, sucrose varies from zero to 60%, and the mannich polyol from 20 to 80%. Of course, the concentrations investigated were much smaller [sucrose 0-30%, ester 20-50%, and mannich 20-40%] and are shown illuminated. The response, Smoke units, is relative to those obtained in the Steiner tunnel.

Smoke levels are affected almost exclusively by formulation amine levels, both in the amine polyol [here at zero] and in the mannich based polyol. The higher the amine content, the greater the smoke levels upon burning.

Using a program such as Design-Expert® allows one to take the data obtained and optimize it to find a best solution. Here we naturally sought a solution having a minimal flame spread and smoke less than 450. One of many solutions predicted is a 45 FS / 400 Smoke foam which can be obtained by using 50 parts of ester, 29 parts of sucrose, and 21 parts of mannich polyol with the fire retardant levels and blowing agent package described above.

Besides good solubility in urethane polyols which affords the formulator desired low viscosity systems, ecomate as the blowing agent also helps the sprayed urethane better wet the substrate, promoting better adhesion. Ecomate is soluble with all other blowing agents on the market, so it can be blended in with other agents to improve their system properties and/or economics.

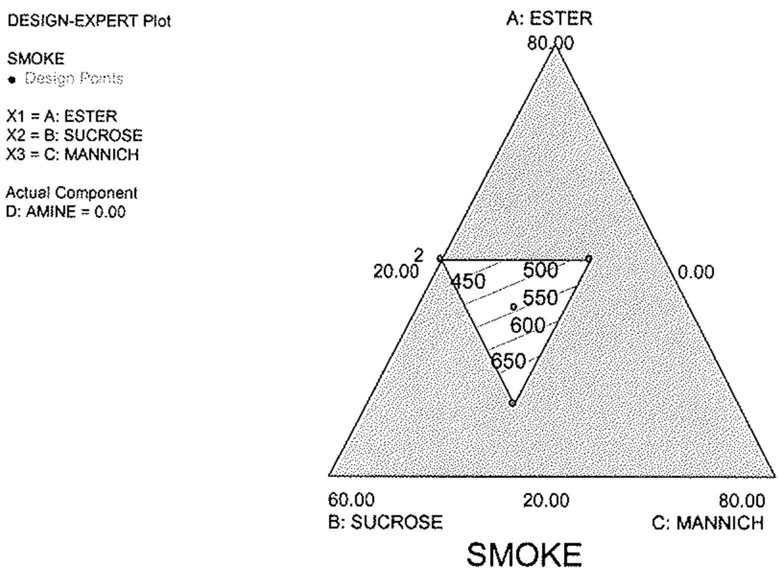

Figure 2: Smoke Levels

Insights:

1. Good indexes are possible using standard polyols with ecomate blowing agent, ranging between 104 and 119.
2. Reproducible 2 pcf, Class II spray foams are easily achieved -
    a. With Flame Spreads under 50;
    b. With low Smoke values below 450.
3. Ecomate quantity has no effect on foam flammability.
4. We have achieved shelf stability with these type systems for well over 3 months
5. All spray raw materials are readily solubilized by ecomate.
6. The best formulation to minimize FS and smoke would have high ester, a generous quantity of mannich polyol, with nearly equal sucrose polyol content.
7. Optimization of the fire retardant package would be the next step to achieving a 25 FS rated foam formulation.

POUR FOAMS

Ecomate systems are dramatically able to achieve good fire resistance. Recently Foam Supplies, Inc's **eco1** pour system was granted by Underwriters Laboratories, Inc. a 25FS / 300 smoke rating at thicknesses up to 6 inches. This same system was taken by one of our customers to Factory Mutual and passed the full scale Corner Wall test.

Since ecomate is rapidly growing in this market segment and is a flammable product, a few comments might help the formulator to fully understand the safe handling guidelines for the product.

While the solubility of ecomate with foam raw materials is excellent, in order to keep the finished system from carrying a red flammable label, formulations should be designed so that there is less than 6 wt%

ecomate in the polyol component, or less than 2 wt% in the isocyanate component. This will usually insure that the mixtures are non-flammable [the best way to discern is to test], and the product can be handled conventionally. Of course, these are merely guidelines, and much depends on the viscosity and the solubility of the resins system one is using as to how fast ecomate will evaporate from the system.

The incorporation of ecomate into batches may be handled in several different ways:

1. The best way of blending ecomate into systems is to mix it into the polyol mixture "in-situ" using a static in-line mixer just prior to drumming off. The high solubility of ecomate easily accommodates this.
2. Another acceptable way of blending is to add ecomate to the polyol mixture in a blending vessel by introducing it into the mixture from the bottom of the tank with agitation.
3. A third method is to have ecomate pre-blended into a major polyol stream at such level as to have its flash point sufficiently high as to avoid danger. This blending can be done as the polyol stream is pumped into the mix vessel, or perhaps bought blended from a polyol supplier.
4. The least favored method of batching is to add ecomate to the top of the batch. This tends to vaporize ecomate, inducing greater loss of material and increasing the opportunity for accident. It also mandates a substantial investment in explosion proof equipment.

Ecomate is an excellent alternative BA for rigid PIR foams, especially where excellent solubility of raw materials is an issue. There is no need to emulsify blowing agents into systems when using ecomate. With ecomate the formulator has the broadest range of polyols from which to choose without any viscosity or solubility constraints. One can obtain good physical properties, perhaps superior properties, with the right choice of polyols.

CONCLUSIONS:

1. Integral skinned foams with the same molding characteristics as achieved by HCFC 141b are easily obtained using ecomate as the blowing agent. Driving this are:
    a. Its excellent solubility,
    b. its perfectly suited boiling point, just above ambient [similar to 141b], which allows good skin formation without expensive cooling,
    c. its benign effect of the environment [non-GWP, non-ODP, and VOC exempt], and
    d. its low molecular weight giving it economical advantage over others.
2. Spray foams made with ecomate give:
    a. good physical properties,
    b. good fire resistance, and
    c. good can stability.
3. Pour foams blown with ecomate have
    a. Excellent physical properties, and
    b. Highest flammability resistance.

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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

[2] US 6,753,357, others pending.

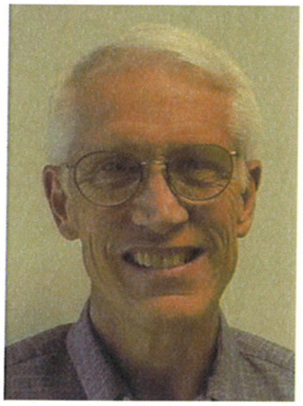
[3] Ref 1

[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

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.