ecomate® Foam Blowing Agent

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ABSTRACT

Foam Supplies, Inc offers a patented blowing agent, ecomate®, for rigid urethane foams. It is an economically and environmentally attractive blowing agent for most urethane foam applications with marketing benefits. Ecomate is a cost effective long term blowing agent solution for the replacement of HCFCs and HFCs.

Four years of field testing have shown this product to be an excellent replacement BA which required little or no formulation change in the finished product, and which maintained without compromise the excellent properties of the original formulation.

Systems formulated with it are very can stable, and the foams made have excellent dimensional stability. Because of its molecular weight and good thermal properties, it offers a very cost effective route to thermally efficient foams.

Foam systems formulated with ecomate have achieved Class I [<25 Flame Spread, < 450 Smoke at 5 inches] flammability ratings under UL723 / ASTM E-84 tunnel testing.

INTRODUCTION

The rigid foam marketplace has undergone many transitions in its existence. One of the most challenging has been the transition through the myriad of foam blowing agents to find suitable products that meet the increasingly stringent environmental constraints placed on the industry. What makes a blowing agent suitable for one industry may make it entirely unsuitable for another. For example, frothing characteristics of gaseous BAs [CFC-12 to HCFC-22 to HFC-134a transitions] are fine for frothing foams, but less desirable for spray foams. Thus, the PU market has been fragmented by the blowing agent requirements of specific products.

Those markets which in the past have traditionally used liquid blowing agents [CFC-11 to HCFC-141b transitions] generally prefer to use liquids in the future. The current choices available in the US as liquids all seem to have some major constraints: Water is an obvious choice, but as a drop-in replacement it has shrinkage problems, the need for very low viscosity polyols, and is disadvantageous for thermal conductivity over not-in-kind insulations.

HFC-245fa, when mixed into a polyol blend, behaves like a liquid, but needs to be handled like a gas prior to mixing and has added constraints in handling [mixing] in the plant and laboratory. While it offers excellent thermal conductivity, has minimal effect on formulation flammability, and meets ODP requirements, HFC-245fa has issues in having a relatively high GWP and very high raw material cost.

Hydrocarbon blowing agents have flammability issues, as well as VOC limitations. These tend to preclude use in non-containment areas as well as in certain market segments such as spray foam. Solubility of certain polyol types with these BA candidates also offers challenge for the formulator. While certain market segments can handle the flammability issues arising in manufacture, storage, and application [by retrofitting their plants], others have difficulty maneuvering around the higher flammability of the finished product [e.g., spray foams].

Because of all these constraints [Liquid vs. gas, VOC, ODP, GWP, flammability, solubility, and cost], the formulator has been both harried and hard-pressed transforming product lines into the best possible solution to utilize current BA offerings.

THE BREAKTHROUGH

Foam Supplies, Inc offers a patented blowing agent, ecomate™, for rigid urethane foams. Ecomate is an economically and environmentally attractive blowing agent for most urethane foam applications with marketing benefits. Ecomate is a long term, cost effective blowing agent solution for the replacement of HCFCs and HFCs.

PHYSICAL PROPERTIES

Ecomate is a clear colorless liquid [Table 1], which has zero ozone depletion potential [ODP] and zero global warming potential [GWP]. While ecomate is a flammable liquid with a Flash point of -26˚ F, [with a LEL of 5% and UEL of 23%], its vapor pressure at room temperature [77˚ F] is only 11.4 psig. Ecomate is not a hydrocarbon blowing agent. It is an exempt VOC with EPA.

Table 1: ecomate® Blowing Agent Properties

Aspect	Colorless Liquid
Boiling Point	89˚ F
Specific Gravity	0.982
Molecular Weight	60
Flash Point	-26˚ F
LEL	5 %
UEL	23 %
Vapor Pressure [psi @ 77˚F]	11.4
ODP	ZERO
GWP	ZERO
VOC	EXEMPT

Table 2: ecomate® Solubility

Chemical	Aspect w 20% ecomate
Polyester Polyol	Clear
Sucrose glycerin Polyol	Clear
Glycerine Polyol	Clear
Amine Polyol	Clear
Mannich Polyol	Clear
Isocyanate	Clear
DEG	Clear
TCPP	Clear
Br FRA	Clear
Prop. Carbonate	Clear
Water	Clear

For the formulator, ecomate is a liquid blowing agent with a boiling point of 89 F, a specific gravity of 0.982 and a molecular weight of 60. Ecomate is sufficiently compatible with most of the resins [polyether, polyester or others] currently used in the industry to facilitate formulation. This can be seen in the data in Table 2 in which all materials remain clear while utilizing more than enough ecomate to achieve density below 2 pcf. In systems, ecomate offers better cost per R-Value than other alternatives to HCFC-141b.

FLAMMABILITY

Flammability aspects of a material or product can be considered from two major positions – OSHA and DOT.

OSHA regulations [29CFR1910.106] take precedence in the handling and storage of materials. A flammable Liquid is defined as any liquid having a flash point below 100 F. A combustible Liquid is defined as any liquid having a flashpoint at or above 100˚ F, which are divided into two classes as follows:
Class II liquids shall include those with flash points at or above 100˚ F and below 140˚ F. Class III liquids shall include those with flash points at or above 140˚ F.

For transportation of materials, the DOT regulations [49CFR173.120] take precedence. A Class 3 flammable liquid has a flash point <141˚ F, and a combustible liquid has a flash point > 141˚F and < 200 ˚F. Packing groups are assigned by the following criteria:

Packing group	Closed Cup Flash Point	Initial Boiling Point
I	<141 ˚F	≤95 ˚F
II	<73 ˚F	>95 ˚F
III	≥73 ˚F, ≤141 ˚F	>95 ˚F

However, final determination of flammability is left to the shipper based on such factors as flashpoint, quantity of material to be shipped, mode of transport, shipping container, etc.

ECOMATE SYSTEMS

Liquid polyol or isocyanate systems made with up to 6 wt % ecomate can be classified as OSHA Class II or Class III combustible liquids, having very low emissions [only exceeding the LEL <2" above liquid level in the headspace of an agitated drum, and not exceeding the LEL anywhere above the open bung of this drum at 85 to 90 F]. Vapor pressures of A-components containing ecomate have been measured at 6 psig at 140 F [Figure 1]. Similar pressures are seen in B-components at the same temperature [Fig. 2]. This means that ecomate systems can be transported in standard [X or Y rated] drums or 16 psi totes without fear of excessive bulging.

FIELD TESTING

Four years of field testing have shown this product to be an excellent replacement BA which required little or no formulation change in the finished product, and maintained the excellent properties of the original formulation without the need for modifications to wall thickness or compressor size.

For example, Table 3 shows that ecomate blown systems have good compressive strengths and good cold and humid aged dimensional stabilities.

STABILITY

Systems formulated with ecomate are very shelf stable as indicated by the results of the ambient and heated aging experiments shown in Figs 3 & 4. Here the formulated system was aged [either at ambient or 120 ˚F] for the time indicated, then cooled to 77 ˚F and hand mix reacted.

Table 3: Physical Properties with ecomate

PROPERTY	ecomate 3-95-1.7	Density	ecomate 2-90-1.7	Density
CS //, psi	45.9	2.3	40.6	2.1
CS_|_, psi	31.1	2.3	27.0	2.0
DIM STABS				
COLD, 7d	-0.06	2.3	-0.06	2.2
HUMID, 7d	2.0	2.2	-0.21	2.1

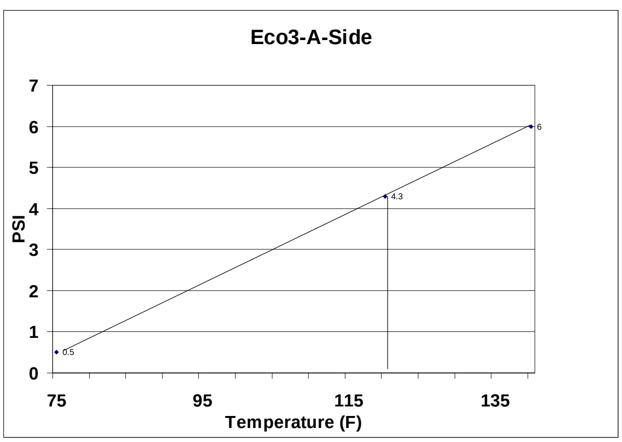


Figure 1. Ecomate in A-Component

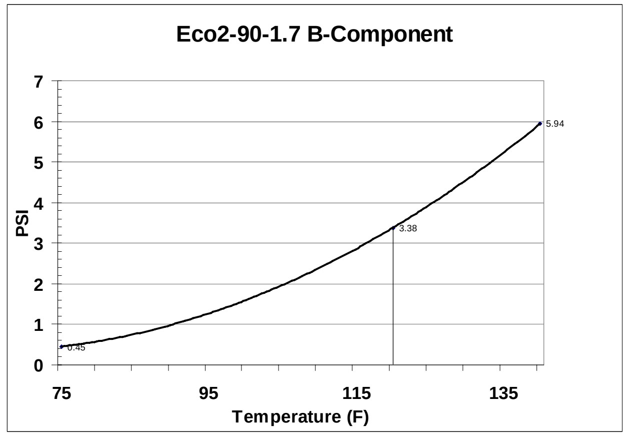


Figure 2. Ecomate in B-Component

Table 4: Fire Resistance with ecomate

INGREDIENT	SYSTEM A		SYSTEM B	
Lot #	04B73		04B77	
POLYESTER	23.7		39.9	
POLYETHER	8.4		10.8	
VISC MOD	5.6		9	
SURFACTANT	1.1		1.8	
FIRE RETARDANT	14.7		14.4	
AMINE CAT	0.1		0.2	
METAL CAT	1.5		1.2	
		Mols of BA		Mols of BA
H2O	1.3	*0.140*	1.4	*0.150*
134a	3.5	*0.034*	10.8	*0.106*
ecomate	1.8	*0.029*	0	*0.000*
Total moles BA		*0.203*		*0.256*
DENSITY, FREE RISE	1.47		1.64	
INDEX	200		180	
FS	25		25	
SMOKE	250		250	

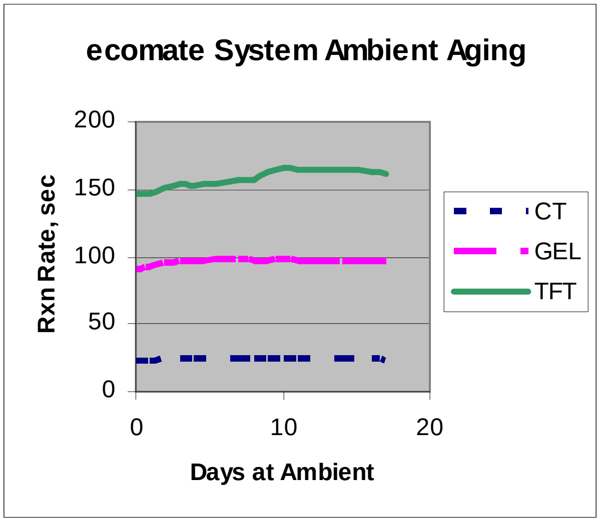


Figure 3. Ambient Aging

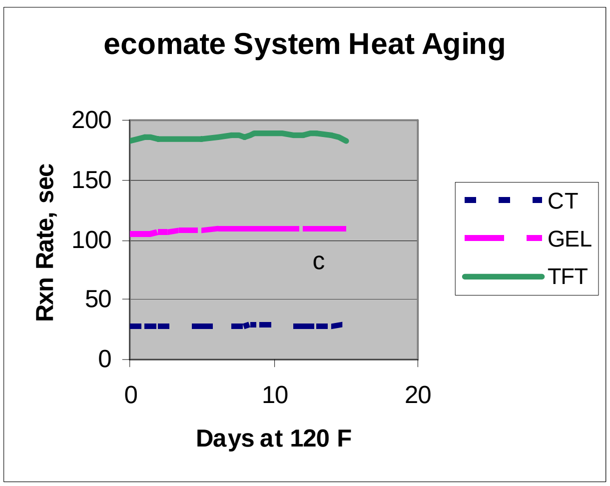


Figure 4. Heat Aging

THERMAL PROPERTIES

Because of its molecular weight and good thermal properties, ecomate offers a very cost effective route to thermally efficient foams. While ecomate is a smaller molecule than the fluorochemicals commonly used, foams made with ecomate show less surface densification, better density distribution, and have better flowability than foams made with other BAs. Field testing has shown that foams having high stress areas, such as at corners or thin sections, generally have poorer thermal retention in those areas. Since foams made with ecomate flow better, they show less thermal loss in critical areas.

FLAMMABILITY

Foam systems formulated with ecomate have achieved Class I [≤25 Flame Spread, < 450 Smoke at 5 inches] flammability ratings under UL723 / ASTM E-84 tunnel testing.

System A shown in Table 4, is a pour-in-place foam system designed for thermal entry doors with 15, 30 minute and 1 hour ratings blown with ecomate, water and 134a. It was poured to a thickness of 6 inches and the skins removed, leaving a 5 inch core for fire testing. System B was made in the same fashion, but used water/134a as the BA. System A has a 20% lower molar BA content, and yet despite this the ecomate is more efficient affording a 10% lower free rise foam density.

Both of these systems were burned in the Steiner Tunnel [ASTM E-84] and achieved identical flame spread and smoke ratings at the 5 inch thickness mentioned above [FS ≤ 25; Smoke = 250]. This experiment demonstrates that ecomate has no deleterious effect on foam flammability as is often seen with hydrocarbon BA candidates.

COST EFFICIENCY

To be truly cost effective, a BA should be economical in its own right, require minimal or no facility changeover for handling and safety, and be thermally efficient enough to not require thickness changes [and the requisite re-tooling] in end-product design.

While some of the changes to accommodate the new BAs may be one-time expenditures, e.g.: pressurized tanks, retrofitting for flammable or combustible materials, or refrigeration units needed to use ‘pseudo-liquid’ BAs, there are some long term considerations to the use of these new materials.

For example, the cost of using a refrigeration unit must enter into the overall cost of the product. The higher cost of ancillary items and safety related items, and the extra precautions that must be employed while using flammable materials also enter into their cost.

In Table 5 below, the mole weight of each material was divided by the mole weight of 141b [i.e.: 117] to show what the relative usage amount of each material would be as compared to141b to blow an equivalent density. The raw material cost is then multiplied by this factor to obtain a relative \$/mole for each BA. This is the cost of a given blowing agent to blow approximately the same density when replacing any other blowing agent.

As mentioned earlier, ecomate blown foams are generally more efficient than other blowing agents. Note the comparison of system A vs. system B in Table 4.

As can be seen in Table 5, only normal pentane is similar on a molar basis. However, due to the aforementioned blowing efficiency of ecomate, much less ecomate is needed to achieve the same density making the true cost of ecomate systems up to 30% less than pentane.

The use of flammable blowing agents presents certain handling risks, starting with bulk storage, pumping, mixing, foaming, storage of finished goods, labeling of containers, and transport. With ecomate that risk is lessened because it is less volatile than hydrocarbons. When mixed with polyols, ecomate has a much higher loading limit before making a mixture red label.

Table 5: 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-134a	▲▲▲	102	0.87	+ 70 %
cC5	▲▲	70	0.60	- 45 %
nC5	▲	72	0.62	- 70 %
ecomate	▲	60	0.51	**- 65 %**

* based on commercial prices 5/27/05

In spite of all the good one can say about ecomate, it may not be a simple drop-in for other blowing agents depending on formulation. However, it can be successfully formulated into pour-in-place, spray foam, and rigid boardstock formulations. As mentioned earlier, Class 1 fire ratings have obtained [ASTM E-84 having 25 FS / < 450 smoke ratings] on some of these types of formulations. The following examples will demonstrate the utility of ecomate in systems [for example, in PIR boardstock].

PIR BOARDSTOCK

Because of the high quantity of ester currently used in a PIR boardstock formulation, and the insoluble nature of the pentanes for the esters used, emulsion technology must currently be used to compatibilize the two. Because of the flammable nature of the HC BAs, higher amounts of FRA [fire retardant additive] and higher indexes have been required to achieve the desired fire ratings.

Ecomate affords the formulator currently using pentanes the opportunity to a lower flammability product, using lower amounts of fire retardant additives and with lower index, having better solubility for the requisite raw materials without the need to emulsify the BA into the formulation with equal or better thermal resistance properties than currently obtained. All the formulations tried in this paper were crystal clear, without any haze.

Ecomate is a slightly stronger solvent for foams than other blowing agents currently on the market, including HCFC 141b. Because of this, ecomate is not a simple drop-in replacement for these other BAs. On the other hand, it gives the formulator more latitude in his choice of raw materials. For instance, one can use higher viscosity [and, if desired, higher functionality] polyols with ecomate and maintain low viscosity B-components.

Flame Spread and Smoke values obtained in the following tables are derived from a modified Monsanto Tunnel with the capability of measuring flame spread and simultaneously capturing light obscuration. Results are relative to the results obtained in the full scale test by calibration. The test unit is calibrated daily with a known sample of isocyanurate board having FS=20 and smoke of 95 per inch thickness. The unit is marked at 25 FS, with inch gradients above and below the 25 FS mark. Smoke is calibrated on the area under the smoke obscuration curve, as is done in the full scale E-84 test. Units obtained are relative to the standard, and like the full scale test may not indicate what may happen in a real fire situation. In the results obtained here:

1"< 25 is ~20 FS; 1"> 25 is ~35 FS. Smoke values > 16 would exceed 450 Smoke in the E84 tunnel.

Table 6: PIR Foam 2.25% FRA [w/wo H2O]		
I=375	**39-3**	**39-4**
Ester 1	10.2	21.35
Water	0.8	0
Ecomate	2.0	7.56
Ratio / 100 A	23.7	54
FLM SPREAD	2" < 25	2" < 25
SMOKE	10.2	1
SHRINK	NO	YES
% WT LOSS	5.4	3.3

Table 6 shows a PIR formulation at a 375 Index with FRA with and without the use of water to co-blow the system. While the higher ecomate level helps to improve the ratio of the foam, it is contributory to slight shrinkage in the board. The substitution of water for part of the ecomate on a molar basis does not affect flame spread, but does increase smoke. In addition, it prevents shrinkage.

Table 7: PIR Foam w/o FRA				
I=375	**39-9**	**39-8**	**39-13**	**39-14**
Ester 1	11.0	10.7	13.3	16
FRA	0	0	0	0
Water	.8	.6	0.4	0.2
Ecomate	2	4.4	5.6	7.0
Ratio / 100 A	20.6	24.0	29.8	36.6
FLM SPREAD	25	1" >25	3" >25	3" >25
SMOKE	22	10	28	26
SHRINK	NO	NO	SLT	YES
% WT LOSS	8	7	11	11

Table 7, using a non-fire retarded formulation, demonstrates that one can vary water / ecomate levels and achieve an optimization of fire properties and minimize foam distortion The optimum level here seems to be about 0.6% water in the entire formulation to achieve low smoke levels, good flammability resistance, and minimal weight loss and shrinkage. The fire retardant was purposefully omitted to show differences that may be too subtle to see with FRA.

TABLE 8: PIR Foam w/o FRA [0.6 % H2O]		
I = VARIABLE	**39-8**	**44-1**
Ester 1	10.7	25.7
FRA	0	0
Water	0.6	0.6
Ecomate	4.4	4.4
Ratio / 100 A	24.0	51.6
INDEX	**375**	**225**
FLM SPREAD	1" >25	2" >25
SMOKE	10	23
SHRINK	NO	NO
% WT LOSS	7	18

Lowering the index [Table 8] from 375 to 225 [still with no FRA] has a greater effect on smoke than on flame spread, though both deteriorate w/o FRA. Weight loss is also negatively affected, while there is no effect on shrinkage using the 0.6 % water co-blow.

As we all know, not all polyols are created equal. This is especially true of esters. Table 9 demonstrates the huge variability in FS, smoke, and weight loss when using different esters. Still, shrinkage is nonexistent using the suggested co-blown scenario.

Table 9: PIR Foam w/o FRA			
I = 225	**44-1**	**44-3**	**44-2**
ESTER 1	25.8		
ESTER 2		23.2	
ESTER 3			29.2
FRA	0	0	0
Water	0.6	0.6	0.6
Ecomate	4.4	4.4	4.4
Ratio / 100 A	51.6	45.9	59.9
FLM SPREAD	2" >25	1" >25	**8" >25**
SMOKE	23	25	34
SHRINK	NO	NO	NO
% WT LOSS	18	17	27

Three additional esters were investigated using the same co-blowing package, but now employing 2.25% fire retardant at a 225 index. The respective properties of Esters 4 to 6 are shown in Table 10. These esters vary in functionality, % aromaticity, and equivalent weight, yet are from the same starting material. Smoke and weight loss were dramatically affected, and increasing values seem to most closely correlate with decreasing equivalent weight, or increasing OH number of the ester. This was unexpected, but may be related to an increased steric hindrance with higher OH preventing trimerization. Flame spread was only minimally affected. There was no evidence of any shrinkage in these formulations.

Table 10: PIR Foam w FRA [0.6% H2O]			
ESTER	4	5	6
EQ WT	303	211	160
FUNC	2.0	2.3	2.2
% AROM	33	37	36
FLM SPREAD	25	1" >25	1" >25
SMOKE	4.2	7.5	9.1
% WT LOSS	4.8	5.7	7.0
SHRINK	NO	NO	NO

CONCLUSIONS

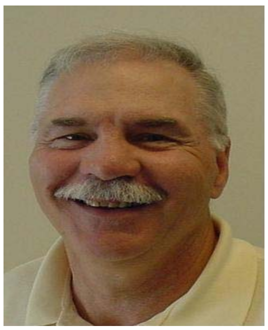
Ecomate truly is a liquid blowing agent, which produces foams with less surface densification, and better, more uniform density distribution, and better flowability than foams made with other BAs. Ecomate has no deleterious effect on foam flammability as is often seen with hydrocarbon BA candidates. It is environmentally [zero ODP, GWP, VOC], and economically attractive for most rigid urethane foam applications. It is a long term, cost effective blowing agent for the replacement of HCFCs and HFCs.

BIOGRAPHIES

John 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.

Buck Green



Buck received his BS in Business Administration in 1975. During his 39 years in rigid urethanes, he has been employed with Mobay [Bayer] and Foam Systems Corp & Stepan Co. Currently employed by FSI, he is responsible for Engineering, Technology, and Product stewardship.

Mark Schulte

Mark received a BS in Chemistry in 1975 from the University of Minnesota, Duluth. He has been in charge of all chemical and regulatory issues for FSI for the past 18 years.