

ENVIRONMENTAL ADVANTAGES OF PENTANE AND NIK BLENDS

John Murphy

Foam Supplies, Inc, Earth City MO 63045 USA

Tel: +1 314 344 3330 Fax: +1 314 344 3331 email: jmurphy@foamsupplies.com

Dennis Jones

The Linde Group, Chertsey Road, Windlesham, Surrey, GU20 6HJ, England

Tel: +44(0) 777 444 8479 Fax: +44 (0) 777 444 8479 email: dennis.jones@boc.com

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.

ABSTRACT

This paper will review the current EU Legislation regarding the GWP and VOC ratings of blowing agents. A quick review of BA options, both present and future, will be covered, including HFC, HFO, HC and NIK blowing agents.

We will show how BA combinations can be used to lower formulation cost, yet improve thermal performance of your systems, all while lowering GWP and VOC content of these systems.

We will demonstrate commercial applications in the arenas of flexible foam, integral skinned foam, rigid PUR pour-in-place, spray, and PIR laminate foams, as well as in commercial refrigeration.

INTRODUCTION

The impact of environmental factors [such as ozone depletion, global warming, in addition to an increasingly keen awareness of smog production], and an ever increasing need to conserve the world's energy resources, have driven the need for efficient insulation in homes, businesses and in appliances. This drive continues, challenged by tighter and tighter legislation regarding GWP and VOC ratings, especially in the EU and in North America.

In 2005, the UK had installed 143 million m² of insulation. Of that 23% was polyurethane insulation, and 8% was extruded polystyrene [XPS]. This will eventually become waste when these buildings reach their end-of- life. Market share is expected to remain much the same in the future as legislation calls for increased insulation standards for buildings in 2012 and 2015. The insulation market is expected to triple by 2020. By that year, approximately 5.0 million m³/year [138,000 tonnes] will become insulation waste. This represents a huge legacy of CFC, HCFC, and HFC gases that for the most part will escape into the atmosphere.

ARE WE THERE YET?

The history of these BA conversions has been well covered by many writers in the past. Needless to say, the successive substitutions have resulted in poorer and poorer insulation potential [Table 1: Impact of BA Changes].

Table 1: Impact of BA Changes

Blowing Agent	Optimal Foam λ , mW/MK	Thickness for same insulation, in
R-11	15.8	1.0
R141b	~20	1.3
R245fa	~22	1.4
CO ₂	34.5	2.2

Currently only HFCs and HCs are being utilized in developed countries, whilst HCFC-141b & HCFC-22 are still allowed in developing countries. HFC banishment is fast approaching. **No, we are not there yet!**

The current options for Blowing Agents in the EU are listed in Tables 2 & 3. Future potential BAs are described in Table 4.

These potential next generation BAs [Table 4] may eventually come to market, if they pass toxicity testing. Although we do not yet know the exact properties of each of the molecules, we do know that the HFOs [hydro fluoro-olefins] above can be readily made from HFC-245fa [US patent application 20050247905]. It is likely that AFA-L1 could be made from HFC-365mfc, by a similar process. FEA-1100 is more likely an ether, rather than an olefin.

While these materials have much improved GWP values, they are still inferior to ecomate®. Their price should be in the same ballpark as the HFCs from which they were derived. That, combined with their high MW, will certainly put them in the same expense category as the HFCs they might replace. Additionally, they may not be able to get VOC exemption status since olefins have, as a class, very high MIR values. With merely the equivalent lambda values as their predecessors, one must ask **is it worth the extra cost just to have non-flammability?**

Table 2: Comparison of ecomate to some HFCs currently available

	ecomate	HFCs		
		245fa	134a	365mfc/227ea 93/7%
MW	60	134	102	150
BP, C	32	10	-26.2	30
Lambda	10.7	12	14	10.7
Flash Pt, C	-32	NONE	NONE	NONE
Sp Gr	0.982	1.32	1.22	1.28
ODP	0	0	0	0
GWP	0	900	1300	820
VOC	EXEMPT	EXEMPT	EXEMPT	n/a

PENTANE & NIK BLENDS

For the sake of clarity, in this paper a not-in-kind [NIK] blend is one which involves a blend of two or more different types of materials. For example, blending a HC with an HFC would be considered a NIK blend.

In the past the notion of blending blowing agents has only been broached when a particular BA would not meet all of the properties required. It is very common to blend a small amount of a gaseous blowing agent with a liquid blowing agent in spray foams, for instance, to garner insulation from a cold substrate by the frothing action of the gaseous additive.

Even more commonly, **blends of pentanes** are used in PIR laminate boardstock to improve solubility, get a more rapid rise, or obtain a lower [better] thermal conductivity. For instance, when the conversion from HCFC-141b to HC took place, that industry segment converted to n-pentane because of cost. They quickly noted that thermal values were poor, so they added a portion of cyclo-C5 to bolster lambda. Then it was noted that the foams reactivity suffered because of the higher BP of the cC5. Trying to overcome that deficiency with catalyst proved costly and frustrating. So ternary blends of nC5, cC5 and isoC5 became common. The issue of solubility was addressed; the issue of slower rise [crème] time was addressed; and the issue of poor lambda was addressed.

Not all segments of the industry can afford the handling of explosive materials, such as pentanes. The cost of retrofitting a plant to be explosion-proof is too dear for smaller production quantities.

Table 3: 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	°C
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	°C
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	

Another reason for blending blowing agents might be **improved flash point**: HFC-365mfc and HFC-227eea is such an example – the addition of 227 improves the flash point of the neat 365.

Environmental pressure or cost might also drive the blending of HFCs with HCs, for instance. Certainly the cost of HCs is much lower than that of the HFCs. It certainly would be an improvement in global warming to lower the GWP values perhaps 5 fold. So why is this not happening?

For one, the solubility for polyols and other additives would certainly be worsened with the addition of HCs. Two, the explosive nature of the HCs is a tremendous impediment. Handling, storage, & blending will all be issues. Three, and most importantly, the insulative capacity of HCs are poorer than the HFCs they are replacing. It would be a mistake to create a poorer product when all your competitors are striving for superior lambda values. Bottom line: poorer solubility, poorer lambda, and potentially explosive mixtures [albeit lower cost and superior environmental properties] are less enticing than status quo.

On the other hand, if you were blowing with HCs exclusively, there is very little drive to improve thermal conductivity if it encompasses the onus of higher cost and worse environmental properties. Low cost is the reason you went to HCs in the first place!

Ahh! But there is an answer! Ecomate®. This environmentally benign [zero ODP, VOC exempt] blowing agent has negligible GWP as compared with HFCs, or even HCs for that matter. Its cost is far less than HFCs; and its usage level is less than half that of the HFC it replaces. Not to mention its gas lambda values are equivalent or superior to the HFC it might displace. It is completely soluble in all the HFCs, not to mention superior solubility with all the raw materials currently used. It is VOC exempt [like the current HFCs] so its introduction into formulations will have NO Effect on smog production. So why is it dismissed single-handedly?

Some fear flammability. Ecomate is about as flammable as was 141b. Ecomate systems can be shipped as 'Non-Hazardous', while pentane systems are 'Hazardous'. Ecomate gives off less energy than MeOH when it burns. Its lower explosive limit is 50,000 ppm in air, five times higher than n-pentane. And when blended into polyol or isocyanate, it does not produce a flash point lower than 35C when used by itself – even when used at levels needed to produce the very lowest of insulation foam densities. When blended into HFCs, the prospect of flammability is lower still, because the halogens present help improve flash point. And unlike HCs, addition of ecomate into a system will NOT require additional fire retardant over current use levels to pass stringent fire tests.

TABLE 4: Potential New BAs [4th Generation]

	FSI	DuPont	Honeywell / DuPont	Honeywell	ARKEMA
	ecomate	FEA1100	HFO1234yf	HBA1 HFO1234ze	AFA-L1
	HCOOCH3	CF3CF2CH2-0-CH3	CF3CF=CH2	CF2H-CH=CF2	CF3CH2CH=CFH
MW	60	164	114	114	128
normalized MW	1	2.7	1.9	1.9	2.1
# F	0	5	4	4	4
%F	0	58%	67%	67%	59%
BP	32	25	-29	<-15	<30>10
Lambda	10.7	10.7	13 ?	13	10
FLASH PT	-32	NO	NO	NO	NO
LFL	5	NO	NO	NO	NO
UFL	23	NO	NO	NO	NO
ODP	0	0	0	0	0
GWP	0	5	4	6	<15
VOC	EXEMPT	?	YES?	YES?	YES?

Some fear instability. Our ecomate systems are extremely stable – having the same reactivity profile for up to one year. This is longer than most systems currently in the market. We have worked hard to achieve this, and the results are covered by patents pending. We are keen to share that with others via Non-Disclosure Agreements.

Some fear loss of market share. They have a vested interest in promoting their special HFC, and would not openly suggest blending with ecomate. Knowing its worth however, Honeywell applied for a patent using 245fa with ecomate [US PATENT APPLICATION 0060160911].

Some fear the unknown. The use of ecomate, whether used neat, or in conjunction with an HFC is fairly straight forward. The conversion from CFC-11 to HCFC-141b took a few years because it was NOT a direct drop in. It was more solubilizing than R11, and that caused people initial consternation. It took the industry nearly 2 years to convert, and it was the only game in town. Ecomate is very much like 141b: in its solubility, boiling point, and flammability.

We now know that HFCs are slated to be replaced, possibly with HFOs or HFEs, depending on a number of unresolved issues [such as toxicity, performance and environmental impact]. We speculate that the prices of these new materials will be at least as expensive as the HFCs from which they will be manufactured. Now might be an ideal time to trial ecomate, either neat or blended with these 'NEXT Generation' products.

PENTANES AND ECOMATE

What are the driving forces here? **Cost?** Not really, since the cost of these materials are in the same realm. However ecomate is not tied to the price fluctuations of petrochemicals, because it is made from MeOH. So ecomate tends to be more cost stable: it resists price increases more readily.

Ecomate is **VOC exempt**. HC's are not!

A relative assessment of smog formation by various chemicals was produced by the University of California, Riverside and expanded to become the Maximum Incremental Reactivity scale of airborne chemicals. This MIR scale is a way of assessing the relative potential of a chemical to produce smog if emitted to the air on a gram/gram basis. The MIR values of pentanes and ecomate are shown in Table 5. Transition to neat ecomate could make a urethane system saleable in Smog Containment districts, thus providing sales [and jobs] that might otherwise be lost.

Table 5: MIR values of Pentanes v Ecomate

Compound	MIR Value
Methyl Formate	0.06
n-Pentane	1.54
iso-Pentane	1.68
cyclo-Pentane	2.69

Ecomate is **less flammable** than HCs. For the sake of emphasis: Ecomate is about as flammable as was 141b. Ecomate systems can be shipped as 'Non-Hazardous', while pentane systems are 'Hazardous'. It gives off less energy than MeOH when it burns. Its lower explosive limit is 50,000 ppm in air, five times higher than n-pentane. Use with HCs can help improve flash point of the HC system.

Ecomate has a **lower BP** than all the pentanes except iso-pentane. Ecomate addition to a formulation allows pentane systems to start to blow at a lower temperature than n- or c-C5. This alone might save the formulator additional catalyst costs.

Ecomate has a **lower molecular weight [MW]** than any other blowing agent currently on the market. This means that less is needed to achieve a given density – it is most efficient. When blended with HCs, its efficiency and low cost are in tune with the low cost philosophy of the wholly HC blown system.

A big plus for the pentane blown system is the **improved solubility** that ecomate can bring to the system. Most pentane systems are initially cloudy and will separate within hours of being mixed. This limits the utility of these systems; they either have to be constantly agitated in a day tank or must utilize a special surfactant to keep the BA emulsified. They also are viscosity limited in the choice of the raw materials, and in materials that are partially solubilized by the HC.

For instance, using pentane alone limits the choice of polyesters that a PIR boardstock manufacturer can use to phthalic anhydride esters. Because this ester is the most soluble [least aromatic] of the ester types in HCs, it is the hardest to fire retard. It requires at least 15% more retardant [more cost] to pass the same tests as foams made with aromatic esters. The use of ecomate can improve solubility of the HC system, allowing the use of more viscous raw materials, especially higher aromatic esters, and elimination of any emulsifying surfactant.

Looking at this in a different way, the component viscosity of the polyol component will be lower with the insertion of ecomate into a HC system. This lower viscosity will allow a better mix of materials, and will produce an extremely fine celled foam. In certain drop-in substitutions, the lower viscosity has resulted in an inadvertent ratio change because the polyol component pumps so much more efficiently with ecomate.

NEAT ECOMATE

Ecomate is being successfully [commercially] used in the manufacture of **flexible slabstock foam** as a direct molar replacement of methylene chloride or acetone. The foams manufactured had no effect on the requisite properties of good slabstock foam - good hand, low density [1.0 pcf], good ILD and good memory. The use of ecomate in this type of foam actually provides benefits not here-to-fore seen, such as the ability to make new classes of foam, and improves the characteristics of MDI flexible foams. The replacement of these toxic and polluting materials will be beneficial to the environment and save many jobs.

Ecomate is the **best solution** to replace 141b [and HCs] in the production of **integral skinned foams**, because it mimics that HCFC so very well: same boiling point, nearly the same solubility, and nearly the same flammability. Because of these properties, ecomate can be dropped into those formulations at about half the loading used for 141b, to give identical properties as obtained with the earlier BA. A recent convert from HC blown integral skinned foam recently told us that it no longer takes him 40 minutes to blend in the BA, but less than 10 with ecomate; and he “made the best parts with ecomate that he has seen since the ‘80s”

Many companies that had formerly switched to n-Pentane to blow their **PIR laminate foams**, and who had to begin using blended pentanes to improve processing/properties, are now starting to investigate ecomate for the improvements in properties as mentioned above. As expected, they are finding better solubility, a lower viscosity Polyol component, better flow on the laminator, and depending on the amount of isoC5 used, a more controllable reaction profile. They have also discovered that they can save money on FRA while using ecomate. And their VOC emissions have been dramatically lowered.

In previous papers I have discussed at length how ecomate can make **superior pour-in-place insulation**. FSI has been making ecomate blown pour and spray systems for over eight years. These systems are more than competitive with other systems in the market, not only with respect to cost, but particularly with respect to physical properties. Ecomate blown foams have the same physical properties as the systems they compete with. We have shown this in many previous papers. We have also shown previously that ecomate blown foams are very competitive thermally [These foams are used in commercial refrigeration units, beverage dispensers, walk in coolers, and refers]. And they continue making strides over competitive systems.

For example, using ecomate, a leading manufacturer of custom refrigeration equipment has surpassed Energy Star standards by an average of 23.7% on its products receiving the Energy Star award.

With the increasing legislative pressures of producing foams with lower thermal conductivity, and with the familiar products being continuously banished, now seems an ideal time to investigate the use of ecomate, either neat or in blends with the existing or future BA offerings.

CONCLUSIONS

Insulation becomes an increasingly important tool to reduce our dependence on fossil fuels. The conversions from CFCs to HFCs have been well intentioned, but have met increasingly stringent challenges that left them outlawed. We have a new product, **ecomate**, which is zero ODP, has negligible GWP, and does not produce smog. It meets or surpasses the physical and insulation criteria of all currently used blowing agents. It is expected to best the future HFOs in MIR values, in GWP values, in insulation, and especially cost. Ecomate's utility is vast: from refrigeration, to construction, in Integral skin and in flexible foams. It has been proven for you. Now is your time to put it into your products, either neat or in conjunction with your current blowing agent. Stop the fluorocarbon legacy.