



Appliance Foams: Overcoming the Next Blowing Agent Challenge through Optimization

It is important to note that there is no “perfect” blowing agent.

blowing agent.

by **john murphy**

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The appliance industry is rapidly facing another environmentally mandated change in polyurethane blowing agents (BA). This means that the currently used class of blowing agents used in developed countries (HFCs), and their predecessors (HCFCs) still being used in less developed (Article 5) countries face imminent transition.

While the industry has become quite adept at transitioning from one generation of BA to the next, it has not been without tremendous compromise in efficiency and economics, not to mention the tremendous amount of man-hours expended optimizing formulations in making these transitions.

For instance, the thermal insulation capability of each successive generation of BA (**Table 1**) has been poorer than its predecessor. They also have had varied boiling points, solubility, flammability, and stability. These affect foam properties dramatically and increase the challenge toward optimization.

Methyl Formate (based on patented technology) is a good choice as a blowing agent because of its low molecular weight, low gas lambda (**Table 2**), and favorable economics. But it has strong solvency (slightly stronger than HCFC-141b), which (like 141b) can affect dimensional stability and compressive strength if not properly formulated for. Similar optimization is/was needed for both

		Gas Lambda (mW/m-K)	Molecular Weight (g/mol)
CFC-11	Generation 1	8.4	137
HCFC-141b	Generation 2	10.0	117
HFC-134a	Generation 3	13.7	102
HFC-245fa	Generation 3	12.7	134

Table 1: Fluorochemical Blowing Agents

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molecules.

Why is optimization so critical? Many formulators, in their initial evaluations of a blowing agent candidate, simply “drop-in” one or more candidates for the original BA. It has not been evaluated with the proper surfactant (or proper amount perhaps), or the proper polyols (in the case of increased solubility of the BA). This was indeed the case in moving from CFC-11 to HCFC-141b. It took formulators nearly two years to properly address the increased demand on the polyol system introduced by the stronger solubility of 141b.

Another factor that is critical for the efficiency of the foam is the **choice of the right surfactant**. The surfactant influences the cell size, orientation, and flow characteristics of the foam—but most importantly the thermal conductivity (k-factor) of the foam! A change in solubility caused by a change of the blowing agent will affect the surface tension of the foam cell windows—and dramatically affect thermal conductivity of the foam. Equally important to the type of surfactant is the amount of surfactant used...to much or too little can result in poorer lambda values.

Optimization is always required.

Even something as mundane as the catalyst package and amount used (speed of reaction) can dramatically affect critical foam properties. The following initial study based on MF blowing agent run by an outside lab dramatically demonstrates this:

Methyl Formate based Appliance System Evaluations – Physical Testing Discussion

Background

The following details outline the runs for the evaluation of initial MF based appliance systems. The objective of the trial was to evaluate standard process and property parameters as part of 1st stage development used to benchmark against existing HFC-245fa based foam systems.

Based on all gathered PT results, the following can be concluded:

- Comparison to standard results:
- ▶ K-factor values for the three systems are higher than what would be expected of a standard HFC-245fa based appliance system.
- ▶ Normalized compression modulus is somewhat comparable to what would be expected, however compression strength is lower than the standard.
- ▶ S1b had slightly better dimensional vac-

	Gas Lambda (mW/m-K)	Molecular Weight (g/mol)
Methyl Formate	10.7	60

Table 2: Blowing Agent

System	Run Date	Comments
MF -S1	11/17	Commercial PIP system
MF-S2	11/18	Alternate Polyol system
MF-S1b	11/19	S1 with increased catalyst

Table 3a: Systems Run

System	S1	S1 @ 77°F	S2	S1b	Standard
Gel (sec.)	50-52	46	40	35	35-40
Tack free (sec.)	71-80	N/A	59-67	55	55-65
Free rise density (lb/ft3)	1.43	N/A	1.43	1.42	1.40
Lanzen Panel					
Minimum fill density (lb/ft3)	2.04	1.99	2.02	1.98	1.94
Flow index (MFD/FRD)	1.43	1.40	1.41	1.40	1.38

Table 3b: Run Summary at 70°F

Properties	Expected value	Comments
Foam Core Density (lb/ft3)	1.80	Range 1.75 - 1.90
Core/Fill Ratio	0.90	
K Factor(Btu-in/hrft2°F) @ 75°F	0.137	Initial value
@ 50°F	0.127	Initial value
“Normalized” Comp strength	19.0 psi	Normalized to 1.80 pcf
Closed Cell Content	90 % minimum	
Dim Stab 14d @ -25°C	-1.70% Vol change	<2% Value required

Table 3c: Physical Testing Summary. Standard “Expected” results for HFC-245fa based system

Name:	Cyclopentane	Methyl Formate	HFO 1233zd[E]	HFO 1336mzz[Z]	UNITS
MW:	70	60	130.5	164	g/mol
Boiling Pt:	49.3	32	19	33	°C
Flash Point:	-37	-19	None	None	°C
LFL:	1.5	5	None	None	Vol%
GWP:	11	< 1.5	< 7	5	100 yr
MIR:	2.39	0.06	0.04	0.04	Ethane = 0.28 g 03/g VOC
PEL:	600	100	300	500	ppm
Gas Lambda:	11	10.7	10	10.7	mW/m²K
sp. gravity:	0.75	0.982	1.27	1.356	g/l

Table 4: Next Generation Blowing Agent Candidates

uum values at 1.85 lb/ft³, therefore free stable density might be somewhere in the range of 1.90-2.00 lb/ft³ core density.

- ▶ Core/fill ratio for the group were in the range of 0.75-0.81 which is below the standard of 0.90. This value is especially important in terms of total foam usage. Higher values are characteristic of more efficient foam usage as it will not require as much foam to achieve a certain core density.
- ▶ Adhesion for these systems was determined to be acceptable and comparable to standard appliance systems.
- ▶ Based on Flow Index, MF systems flow better than the standard 245fa system.
- ▶ Overall, greater cross-linking and running at a higher index would benefit both the dimensional stability of the foams as well as the strength.

Observations between systems:

- ▶ **Addition of catalysis to S1** improved K-factor, cell size, cell content, and normalized compression strength.
- ▶ The same relationship can be seen when S1 component temperature was increased from 70°F to 77°F on run day 1. **Foam cell structure/cell content improved as a result of faster reactivity.**
- ▶ **S1b overall** was the best performing system of the group in all areas of foam performance.

Bear in mind that these were initial investigatory runs made with MF foam blowing agent. MF has a slightly stronger solvency than even HCFC-141. Because of this, formula changes such as greater cross-linking and running at a higher index benefits both the dimensional stability of the foams as well as its strength.

Further optimization of these formulas has demonstrated improved dimensional stability, compressive strength, and thermal properties allowing MF to be competitive with current blowing agents.

Today we are faced with yet another transition, from Generation 3 HFCs to **other alternates** (including Generation 4 HFOs, *Table 4*). It is important to note that there is no “perfect” blowing agent. There never has been, nor will there ever be! Each has its merits and its shortcomings. Each has allowed the polyurethane industry to grow, by **optimization** of formulations for the BA then being used.

The HFOs bring improved gas lambda values back to the table. However, it is not without some challenge, as those candidates

are higher in molecular weight (i.e., more is required on a molar (MW) basis to achieve a desired density). For instance, to produce an equivalent density foam, it would require 130.5 parts of HFO-1233zd versus 70 parts of Cyclopentane—nearly twice the quantity. That, concurrent with an additional disparity in pricing, steepens the challenge. In addition, little is yet known about any potential diffusion of the HFOs from the foam insulation through the plastic liners

into food stored in refrigerators (or of the diffusion of their break-down products, or if any potential toxicity of these break-down materials exists).

The future choice of blowing agents for the appliance industry will require diligent work today to address these unknowns, and to optimize each of the above candidates into successful appliance foam formulations. The time to start is now. May the best candidate win! ■

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