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There have been changes brought on by technology, raw materials, competition and regulations as the industry has become worldwide in its scope. *Photos above courtesy of the author.*

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A BRIEF HISTORY OF CHANGE IN THE REFRIGERATION INDUSTRY

The history of the refrigeration industry has been tied to that of the polyurethane foam industry for decades, and even more closely to that of the foam blowing agents.

There have been changes brought on by technology, raw materials, competition and regulations as the industry has become worldwide in its scope. This paper is an attempt to give an unbiased history of some of the modifications in design brought about by changes in insulation raw materials used in manufacture over the past several decades, and how current regulatory pressures might influence further changes.

The early days of refrigeration started with a mere ice box cooled by a 40-pound block of ice. The next major development that followed was ammonia as the refrigerant, but was discontinued due to safety concerns. Fast-forwarding to more recent years, the use of flouochemical refrigerants such as R-12 (Dichloro difluoro methane) and R-22 (difluoro dichloro ethane) reigned throughout the industry for more than half a century.

The Role of the Blowing Agent

What did polyurethane foam bring to the refrigeration industry? Foam became more than just insulation for the refrigerators, it became the "glue" that held the cabinets together, as well as structural support allowing manufacturers to utilize thinner metals and liners. In addition to having superior insulation values, it allowed a streamlining of the manufacturing process.

The blowing agent used in the polyurethane formulation controls, most importantly, its thermal properties, as well as the viscosity of the mixture before cure, and its flow into the refrigerator unit (hence fill and demold times) plays a major role in solubility of the plastic liner material by the foam. It can also affect the density and dimensional stability of the foam produced (and hence of the

Each blowing agent has its merits and its shortcomings, and each has allowed the refrigeration industry to grow.

by john murphy

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refrigerator itself).

And the blowing agent has a strong influence of formulation cost. The blowing agent is generally used on a molar basis to give equivalent density foam. The same molar content of any blowing agent should give the same number of moles of gas. For example, 40 parts of R-11 with a mole weight of 137 (MW137) could be replaced with 34.16 parts of HCFC-141b (MW117) to give similar density foam. Thus 40/137 = 34.16/117 = 0.292 moles of gas. The lower its MW, the less blowing agent is needed on a weight basis. This can have a definitive effect on formulation cost.

Another factor affecting formulation cost is the number of fluorines on the blowing agent—the greater the number of fluorines, the more expensive that blowing agent will be. The last number in a blowing agent name is the number of fluorines it has. For example: CFC-11 and HCFC-141b each have 1 F; HFC-245 has 5 Fs.

First Generation Blowing Agents (CFCs)

Polyurethane foams became a key player in insulation (and especially in refrigeration insulation) because of the role of Refrigerant 11 (trichlorofluoromethane, (CFC-11)). This liquid boiled at room temperature (75°F) and was non-toxic, non-corrosive, and non-flammable. And most importantly, this foam blowing agent was thermally efficient (with a gas Lambda of 8.4 mW/mK). It allowed foams to be produced that were twice as efficient per inch of thickness as any other insulation then available.

The use of urethane foam allowed the refrigerator manufacturer to use an outer steel shell with an inner plastic liner held together by the urethane itself. This was a major improvement and simplification of the manufacturing process. That, and changes in compressor design, permitted a refrigerator to have a lifetime of 15 to 20 years.

So the refrigeration industry, and the urethane industry, grew because of R-11. It reigned supreme as a blowing agent for three-plus decades.

Second Generation (HCFCs)

In the mid-1980s, global warming became an issue. It was deemed that R-11 was a contributor to global warming and should be eliminated. Two candidates, HCFC-141b and HCFC-123, were offered as potential replacements by the fluorochemical industry. R-123 was subsequently eliminated because it was found to be toxic. R-141b (1,1-dichloro-1-fluoroethane) had a gas lambda of 10 mW/mK (poorer than CFC11), and was a much stronger solvent than R-11 which caused HIPS (High Impact Polystyrene) refrigerator liners to crack. This was mitigated by the use of ABS (Acrylonitrile Butadiene Styrene) liners, and by co-blowing 141b with water, which caused poorer insulation (lambda) values. The refrigeration industry subsequently optimized formulas around R141b, and used it in the United States for over a decade. During that time they began to build manufacturing plants in Mexico and other parts of the world. They continue to build units made with 141b in those locations today.

Third Generation (HFCs)

Ozone depletion became the cry that marked the fall of the HCFC foam blowing agents, and marked the introduction of the HFCs (134a, 245fa, and 365mfc) into the market in the U.S. Other developing countries are still permitted to use HCFCs. These new HFCs have poorer solubility, and poorer lambda values than did 141b. HFC-134a (1,1,1,2-tetrafluoroethane) and 245fa (1,1,1,3,3-pentafluoropropane) are gases at room temperature (RT=75°F). A patent situation restricted the U.S. to ONLY 245fa, and EU to use only 365mfc. (A 93%/7% blend of 365mfc and 227ea was created because 365mfc by itself was flammable.) And when 365 supply became force majeure because of production issues, Europe was allowed (for nearly a decade) the use of 245fa. The U.S. was denied 365 usage until six months ago. Both these HFCs have poorer gas lambda values (lambda 245fa =12.7; Lambda 365mfc = 10.5 mW/mK) than 141b (lambda = 10), and poorer solubility, which allows the industry to use PS liners once again.

Fourth Generation – HFOs and more

The only thing certain in this world is change. A new challenge for foam blowing agents (BAs) is GWP (or Global Warming Potential) status. This means that certain BAs contribute to CO^2 concentrations in the atmosphere, increasing global warming.

The U.S. government has recently mandated transitioning out of HFCs by the end of 2016 (January 1, 2017), while still demanding improved efficiencies and lower energy usage in each refrigerator or freezer unit produced. What HFCs are affected? HFC -134a, 143a, 245fa, and 365mfc, and blends thereof, in addition to Formacels B, TI, Z6 in products manufactured or imported into the U.S. after that date.

There are other blowing agents in addition to those fluorochemicals listed above. Hydrocarbons have been around for decades but were dismissed early on because of flammability. Recently, the U.S. EPA funded the Chinese in developing an all-hydrocarbon (both insulation and refrigerant) refrigerator.

A technology based on methyl formate that was developed as a blowing agent in 1998 and commercialized in 2002 has proven itself in all applications, and

Name	Cyclopentane	Methyl Formate	HFO 1233zd(E)	HFO 1336mzz(Z)	
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	Ethane = 0.28
PEL	600	100	300	500	ppm
Gas Lambda	13	10.7	10	10.7	mW/mK
sp gr	0.75	0.982	1.27	1.356	g/l

Table 1: 4th Generation Foam Blowing Agents

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Even when they're looking in here.

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in the commercial refrigeration market in particular. This technology has been demonstrating its synergy in blowing agent blends long before the fourth generation blowing agents were available. Both of these blowing agents have been around for some time, have proven themselves, and meet all current governmental strictures.

Enter a new class of foam blowing agents: the HFOs. These are compounds that have unsaturation (carbon to carbon double bonds, or C=C) in their structure, so that they readily decompose in a matter of days rather than hundreds of years and thus not cause damage to the environment.

There is no "perfect" blowing agent. There never has been, nor will there ever be! Each blowing agent has its merits and its shortcomings. Each has allowed the refrigeration industry to grow, by optimization of formulation for the blowing agent then being used.

So what are the current blowing agent replacement contenders (Table 1) and what are their strengths and weaknesses?

Two of the materials in this table are not HFOs: cyclopentane and the technology based on methyl formate. In the HFO arena, two companies propose to manufacture HFO 1233zd, while another is championing HFO 1336mzz.

Cyclopentane has shown itself to be the best of the hydrocarbon blowing agents. Its major pluses: it is a fairly effective insulator, and quite cost effective (low price combined with low MW).

Negatives: poor solubility for PU raws, is a smog producer, and explosively flammable (although not a criticality, because some manufacturers are using it!)

Technology based on methyl formate: Advantages: thermally better than cC5; has shown thermal synergy with all other blowing agents on this list; NOT a VOC, nor GWP nor ODP; is far less flammable than hydrocarbons (Non-explosive (with over 50% oxygen in molecule) and does not require red placards when in systems); Is a much better solvent - more like 141b (two edged sword); low price and lowest MW of those listed above.

Disadvantages: High solvency (like 141b) sometimes an issue.

HFO 1233zd(E): Advantages: Not flammable; Low GWP; No smog issues with atmospheric life of 26 days; good thermal properties exhibited; moderate solubility so can use with HIPS.

Negatives: Marginal liquid at RT (BP 19°C); double the MW of technology based on methyl formate and has 3F, so moderate economics; unsaturation may be a stability issue; unproven. Currently available only in small quantities.

HFO 1336mzz(Z): Advantages: good thermal properties; true liquid; not flammable; no smog issues (MIR 0.04), Moderate solubility so can use HIPS; azeotropic thermal advantages with blends shown.

Disadvantages: highest MW and F content will be economically challenging; unsaturation may be a stability issue; unproven. Currently available only in small quantities.

The appliance industry once again is faced with a mandated conversion. This time there are more choices. With the need for more thermal efficiency in the foam, this author believes the future of the fourth generation conversion will be in HFO blends with the smaller molecules such as technology based on methyl formate or cyclopentane, since thermal and economic advantages have already been seen there. Time to start optimizing! ■