

# Alternative Blowing Agents



Blocks of polyurethane foam blown with ecomate blowing agent.

*Global warming issue drives new developments.*

The saga of alternative blowing agents for polyurethane foam insulation seems never-ending, and new chapters are still being written. In both residential and commercial refrigeration applications, the blowing agent CFC-11 had been the standard for years until banned by the Montreal Protocol because of its ozone depletion potential (ODP). Given the challenges of quickly finding ideal alternatives, HCFCs such as HCFC-141b, with a somewhat lower ODP, were approved as a temporary alternative until better blowing agents could be found.

With the eventual mandated phase-out of that chemical, manufacturers diverged down one of two paths — hydrocarbons or hydrofluorocarbons (HFCs). Those concerned about the flammability of hydrocarbons selected one of several HFC options. But as global warming has risen on the political and public agenda, the high GWP values of the HFCs have raised questions about their long-term future as blowing agents and has everybody involved rethinking the issue yet again.

Not surprisingly, this was a hot topic at the Polyurethanes 2008 Technical Conference held in San Antonio, Texas, in September

2008, and the Insulation Options Technical Session featured a number of papers addressing it. Three of those papers are summarized here.

## Arkema

*Investigation of New Low-GWP Blowing Agents for Rigid Polyurethane Foams*, by Ben Chen, Joseph Costa, Philippe Bonnet, and Maher Elsheikh, Arkema, King of Prussia, Pa.; and Laurent Abbas, Arkema France, Pierre-Benite, France.

The need for insulation materials with improved energy efficiency and environmental profiles has led Arkema to investigate a range of low-GWP blowing agents designed for most PUR applications, including appliances, pour-in-place, spray, and PIR boardstock. These fourth-generation blowing agents — the AFA series — are being developed in both liquid and gas formulations to replace HFCs such as 245fa and 134a.

All the AFA molecules have very low GWP values, less than 15, and negligible ODP values. Both AFA-G1 and AFA-G2 have a lower flammability limit (LFL) at ambient temperature. However, AFA-L1 did not exhibit either a flashpoint (FP) or flammability limit under ambient conditions. Both AFA-L1 and

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AFA-L2 exhibit a low gas-phase thermal conductivity (Lambda), comparable to HCFC-141b, which should contribute to the insulation value of the rigid polyurethane foam.

Both liquid and gaseous versions of the blowing agents were evaluated in regards to blowing efficiency, dimensional stability, and insulation properties.

The two experimental gaseous blowing agents, AFA-G1 and AFA-G2, were compared with HFC-134a. The Free Rise Density figures for the gases indicated that AFA-G1 (1.79) showed better blowing efficiency than either the AFA-G2 (2.03) or the HFC-134a (1.98). In terms of dimensional stability both of the experimental blowing agents performed better than HFC-134a blown foam. The shrinkage exhibited for the three blown foams was -5.0 percent volume change for the AFA-G1 foam; -6.4 percent volume change for the AFA-G2 foam; and -17.3 percent for the HFC-134a foam. The k-factor for the three foams was measured over five temperature ranges, with the lowest 18 DegF and the highest 104 DegF. The two AFA foams showed comparable k-factor performance with HFC-134a, with the exception of the coldest temperature (18 DegF), where the AFA-G1 performance was worse than both the AFA-G2 and the HFC-134a.

In tests involving two different foam formulations, the two experimental liquid blowing agents, AFA-L1 and AFA-L2, were compared against HCFC-141b, HFC-245fa, and an 80/20 blend of cyclopentane and isopentane. In the Formulation 1 test, all five foams showed similar blowing efficiency, as indicated by free rise density. Because of the lower density and lower functionality polyol makeup, all the foams showed significant volume change. AFA-L2 expanded the most at 41.8 percent volume change, and AFA-L1 expanded the least at 18.6 percent volume change, roughly 6 percent to 8 percent less than the other three foams. The initial k-factor results for this formulation with the liquid blowing agents showed that both AFA-L1 and AFA-L2 exhibited significantly better k-factor than HCFC-141b, especially at the cold-temperature to room-temperature test conditions. AFA-L1 exhibited a better k-factor than HFC-245fa over all test temperatures; AFA-L2 also performed better than HFC-245fa, but the gap was less, especially at the colder test temperatures. Both of the experimental liquid blowing agents performed much better than

the cyclo/isopentane foam.

In the Formulation 2 test, AFA-L1 alone was compared against the HCFC-141b, HFC-245fa, and cyclo-isopentane. As with Formulation 1 foams, AFA-L1 showed similar blowing efficiency to HCFC-141b, HFC-245fa, and cyclo/isopentane. Due to the higher density and different polyol composition of this system versus Formulation 1, all the blowing agents tested gave similar and acceptable dimensional stability performance. AFA-L1 exhibited similar k-factor performance to HCFC-141b over all the temperatures tested and performed slightly better than HFC-245fa. However, the differences were much less than with Formulation 1. Also, as with Formulation 1, AFA-L1 performed significantly better than the cyclo/isopentane foam.

The conclusions drawn from the testing of the new low-GWP blowing agents suggest that AFA-G1, and to a lesser extent AFA-G2, can potentially compete with HFC-134a in terms of solubility in polyol, dimensional stability, and k-factor, although AFA-G1 seems to perform less well at very cold temperatures.

The more interesting results were found on the new low-GWP liquid blowing agent candidates for replacing HFC-245fa. AFA-L1 displayed a similar blowing efficiency and dimensional stability and a significant advantage on k-factor compared to hydrocarbons.

## DuPont

*Development of a Novel Foam Expansion Agent for Polyurethane Foams*, by Mark L. Robin, Gary Loh, and Joseph Creazzo, DuPont Fluoroproducts, Wilmington, Del.

The regulatory mandated phaseout of HCFC-141b as a foam expansion (blowing) agent for polyurethane foams required the development of Third Generation foam expansion agents such as HFCs and hydrocarbons. While these agents have zero ozone-depletion potential, they have other disadvantages.

The primary HFC expansion agents developed for rigid polyurethane foam are HFC-245fa and HFC-365mfc. Disadvantages of HFCs include their increased thermal conductivities compared to previous generation expansion agents and their high GWP values: HFC-245fa has a GWP of 1,020 and HFC-365mfc has a GWP of 782. In addition, HFC-245fa is characterized by a relatively low

boiling point of 15 DegC, rendering the handling of HFC-245fa and the processing of its foams more troublesome compared to when the foam expansion agent is a liquid at room temperature. HFC-365mfc is a liquid at room temperature, but has the disadvantage of being a flammable compound. Hydrocarbon expansion agents such as pentane, isopentane, cyclopentane, and methyl formate all exhibit low GWP values (Pentane = 11 GWP), but exhibit flammability and thermal conductivities even greater than those of the HFCs.

The ideal foam expansion agents should exhibit the following characteristics:

- ▶ Low vapor thermal conductivity.
- ▶ Nonflammable.
- ▶ Liquid at room temperature (Boiling point greater than 25 DegC).
- ▶ Low toxicity.
- ▶ Zero ODP.
- ▶ Low GWP.
- ▶ Chemically, thermally stable.
- ▶ Soluble in formulation.
- ▶ Low rate of diffusion.
- ▶ Economically feasible.

DuPont Fluoroproducts has developed a novel Fourth-Generation foam expansion agent for polyurethane foams that meets all of those requirements. FEA-1100 is characterized by zero ozone depletion potential, very low acute toxicity, and has a low GWP value of 5. Because it is liquid at room temperature, the problems associated with the use of lower boiling agents such as HFC-245fa are eliminated. In addition, FEA-1100 has been shown to be non-flammable in standard ASTM tests.

Polyurethane foams produced with FEA-1100 are characterized by low foam density, uniform cell size, and R values higher than HFC-245fa. (FEA-1100 R-value @ 75 DegC = 7.1 compared to HFC-245fa R-value @ 75 DegC = 6.6.) Upon aging, the foams expanded with FEA-1100 retain R values higher than those expanded with HFC-245fa.

Similarly, polyisocyanurate foams produced with FEA-1100 are characterized by low foam density, uniform cell size, and R values higher than foams blown with HFC-245fa. (FEA-1100 R-value = 7.7 compared to HFC-245fa R-value = 7.2.) Upon aging, the foams expanded with FEA-1100 retain R values higher than those expanded with HFC-245fa.

While foam expansion agents can be used singly, mixtures of different physical foam

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expansion agents can be useful for optimizing foam performance and meeting customer demands, such as reduced expansion agent flammability, reduced vapor pressure, etc. Polyurethane foams produced with the azeotrope of FEA-1100 and cyclopentane as the foam expansion agent are characterized by low foam density, uniform cell size, and high R values. Initial R values for foams expanded with the FEA-1100/cyclopentane azeotrope are higher than those for foams expanded with cyclopentane alone or neat FEA-1100.

Polyurethane foam employing an azeotrope-like mixture of FEA-1100 and HFC-365mfc as the foam expansion agent are characterized by low foam density, uniform cell size, and high R values. Initial R values for foams expanded with FEA-1100 or the FEA-1100/HFC-365mfc azeotrope-like mixture are higher than those for foams expanded with neat HFC-365mfc. FEA-1100 and mixtures of FEA-1100 and HFC-365mfc also offer the advantage of reduced flammability compared to neat HFC-365mfc.

The conclusion drawn from tests of DuPont's low-GWP FEA-1100 foam expansion agent for polyurethane foams is that polyurethane and polyisocyanurate foams produced with this new agent are characterized by good dimensional stability and uniform cell size. In addition, R values for foams produced using this new foam expansion agent match or exceed those obtained with current generation blowing agents such as HFC-245fa.

## Foam Supplies

*A Comparison of the Physical Properties (and their causative factors) of Froth vs. Pour Foams*, by John Murphy, Foam Supplies, Earth City, Mo.

Since HCFC-22 has been phased out, many manufacturers of urethane insulation panels for the construction and commercial appliance industries are faced with the difficult decision of either staying with a froth type blowing agent such as HFC-134a, or transitioning to a liquid (or near liquid) alternative such as pentane, water, HFC-245fa, or ecomate, a patented methyl-formate use developed by Foam Supplies.

The original appeal of froth formulations is their low boiling point that allows them to emerge from the foam unit with a shaving cream consistency. One of the major disadvantages is the requirement for pressurized

foam dispensing equipment. Boiling point is one of three paramount factors in determining a good blowing agent, the other two being solubility in the resin system and its molecular weight. Other concerns include flammability and GWP values and their inverse relationship. Decreasing halogen content in blowing agents makes them more flammable. A higher halogen content makes them less flammable, but increases their GWP values and overall cost.

A comparison of properties shows that ecomate has a GWP of 0, compared to 1,300 GWP for HFC-134a, 140 GWP for HFC-152a, and 950 GWP for HFC-245fa. In regards to flammability, ecomate has less potential to burn than either n-pentane or c-pentane, and ecomate has better flammability characteristics than HFC-152a. Ecomate can be formulated into polyol systems having flash points for the compounded system greater than 35 DegC, making them safe for shipments without Red Placards.

Decreasing the halogen content in a fluorocarbon can also decrease the solubility of the hydrocarbon base, which results in greater loss of the blowing agent to the atmosphere upon foaming.

In a study performed by Foam Supplies, a polyurethane foam originally formulated for HCFC-22 was substituted on a molar basis with HFC-134a and ecomate. Panels with each were made and tested. A number of conclusions were drawn from the tests.

One, liquid blowing agents are clearly different than froth blowing agents. Liquid blowing agents have lower heats of vaporization — they cool less — and they typically require tighter molds, especially when foaming in a vertical position. At the same time, however, liquid blowing agents produce better flow in molds and better density distribution in the resultant foams.

Another observation was that all formulations require optimization. Froth foams require a high amine polyol content to overcome their cooling effect. Therefore, a liquid blowing agent cannot simply be dropped into a froth formulation because the high amine polyol content will cause the foam to lock up prematurely and create a foam with higher density. A liquid blowing agent system requires a lower amine polyol content to avoid this problem.

In addition, froth foams have greater vapor loss than liquid-based foams, which

is generally bad for the environment; froth foams cost more than liquid foams. The cost of fluorochemicals will always exceed that of the ethers, esters, or hydrocarbons that they are manufactured from, depending directly on the number of F molecules used.

The most important difference, however, is the effects on the environment. Halogen-containing blowing agents are less environmentally benign than ecomate. For example, HFC-134a, with a molecular weight of 102, requires 1.7 times more material than ecomate to blow the same density foam. Multiplying that 1.7 times the HFC-134a GWP value of 1,300 reveals that a conversion to ecomate can spare the environment 1 metric ton of CO<sub>2</sub> equivalents for every pound of ecomate used. ■

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