Evaluation of Low Global Warming Potential Blowing Agent Solutions in Pour-in-place Panel Applications

JIM Y.K. LING
Honeywell International
20 Peabody Street
Buffalo, USA

RYAN S.L. QIN
Honeywell Technology Solutions
430 Li Bing Road
Shanghai, China

ABSTRACT

Insulated metal panels with polyurethane or polyisocyanurate foam cores and rigid facers, such as metal, have been extensively used in cold-chain and construction applications. The industry is actively searching for blowing agent solutions for their products that provide maximum energy efficiency performance and minimum environmental impact. Honeywell has two highly energy efficient and low global warming potential (LGWP) blowing agents: a gaseous blowing agent, 1234ze(E), and liquid blowing agent, HBA-2, which has global warming potential of 6 and 7 respectively. They also are non-flammable and likely to be classified as non-volatile organic compounds in the U.S. Through a “drop-in” blowing agent substitution, physical, thermal and flammability properties, of pour-in-place panel foams with these two LGWP blowing agents, and with 1234ze(E) and its blends with cyclopentane, which also identified as C-C5 in this paper, were evaluated in a system house commercially available formulation and a US-based Honeywell generic formulation respectively. HBA-2 and its blends with cyclopentane were also evaluated in a China-based Honeywell generic formulation.

Foams made with both 1234ze(E) and HBA-2 demonstrated about 4% to 6% better thermal insulation and similar physical properties compared to the 134a and 245fa benchmarks. Moreover, HBA-2 showed superior aged thermal insulation values which exceeded other commercially available liquid blowing agents. The 75/25mol% HBA-2/cyclopentane blend, which provides comparable physical properties and initial thermal conductivity as HBA-2, offers a balanced solution between superior properties and cost. 1234ze(E) appears to be an excellent additive to cyclopentane. The 13/87mol% 1234ze(E)/cyclopentane blend demonstrated similar initial thermal insulation value at low temperature, better thermal insulation retention and improved dimensional stabilities when compared to cyclopentane. Although the evaluated blends are most likely flammable, these blends as well as 1234ze(E) and HBA-2, provide viable LGWP blowing agent solutions for pour-in-place applications which can fulfill the diverse needs of the industry.

DISCLAIMER

Although all statements and information contained herein are believed to be accurate and reliable, they are presented without guarantee or warranty of any kind, expressed or implied. Information provided herein does not relieve the user from the responsibility of carrying out its own tests and experiments, and the user assumes all risks and liability for use of the information and results obtained. Statements or suggestions concerning the use of materials and processes are made without representation or warranty that any such use is free of patent infringement and are not recommendations to infringe on any patents. The user should not assume that all toxicity data safety measures are indicated herein or that other measures may not be required.

INTRODUCTION

Polyurethane foam has been used as thermal insulation in many different applications. One such application is insulated metal panels, which consist of a polyurethane foam core and two metal facers. The panels are used frequently as insulation in building envelope applications in commercial and residential structures, such as cold storage warehouse and big box retailers. Insulated metal panel has also found utility in some cold chain applications, for instance, walk-in coolers, walk-in freezers and insulated trailers. These foam core metal panels can be manufactured by either continuous or discontinuous production methods.

Many blowing agents are being used around the globe. In developed countries, such as the U.S., EU and Japan, both liquid and gaseous third generation blowing agents, such as 245fa, hydrocarbons and 134a are used because of their high-performance attributes and also meeting the requirements of the Montreal Protocol. In contrast, third generation blowing agents and even second generation blowing agents, such as 141b, are used in developing countries, such as China and India, due to the different stage of regulations in these countries. As the LGWP initiative emerges in developed countries and the HCFC phase-out in developing countries approaches, manufacturers' interest in the fourth generation, LGWP blowing agents is growing worldwide.

In this paper, direct comparisons of foam properties among various types of liquid blowing agents, including HBA-2, 245fa, cyclopentane and 141b, were conducted. Compared to the 134a baseline, foam properties with gaseous LGWP blowing agent, 1234ze(E) were also evaluated through the results by a system house in the U.S.. Physical, thermal and flammability properties of foam blown with LGWP blowing agent blends, such as 1234ze(E)/cyclopentane and HBA-2/cyclopentane, were also evaluated. Furthermore, physical properties and toxicity update of both Honeywell LGWP molecules were reviewed.

EVALUATIONS & FINDINGS SUMMARY

Table 1 summarizes "drop-in" evaluations conducted and results discussed in the paper.

Table 1 Evaluations of Foams &Findings Summary

Blowing Agent	Important Findings
HBA-2	Thermal properties and physical properties surpass cyclopentane Better thermal properties and comparable physical properties to 245fa Best thermal properties retention among liquid blowing agents evaluated
HBA-2/C-C5	75/25mol% blend offers comparable physical property to HBA-2 75/25mol% blend provides similar initial thermal conductivity to HBA-2
1234ze(E)	Comparable physical properties as and better thermal property than 134a
1234ze(E)/C-C5	13/87mol% blend offers similar initial thermal conductivity to cyclopentane Blending 1234ze(E) lessens the non-linearity of thermal conductivity Blending 1234ze(E) enhance thermal conductivity retention

DEVELOPMENT SUMMARY

A key raw material in the production of high performance, rigid polyurethane insulation foam is the blowing agent. Although many blowing agent technologies are available to the foam formulation chemist, the use of fluorocarbon blowing agents has historically resulted in foams with the highest insulation performance, best physical properties, safest and simplest processing characteristics, and best value in use. The use of fluorocarbon blowing agents began as early as the mid-1950s with the introduction of trichlorofluoromethane, or 11. This blowing agent became the industry standard until the mid 1990s, when concerns over ozone depletion led to the development of a second generation of high performance foam blowing agents, the HCFCs. For the rigid polyurethane foam industry, the most commonly used HCFC was 1,1-dichloro-1-fluoroethane, or 141b. Although conversion to141b reduced the ozone depletion potential of the blowing agent by 90%, subsequent regulation required that these HCFC blowing agents also be phased out and a third generation of high performance blowing agents were developed, the HFCs. The most commonly used HFC blowing agents in rigid polyurethane foam is 1,1,1,3,3-pentafluoropropane, or 245fa. This material satisfied the requirements of ozone depletion regulation while, at the same time, retained the high performance and non-flammability required in many foam applications. In many parts of the world, conversion from HCFC technology to HFC technology is complete while, in certain other regions, this conversion is now occurring.

In recent years, concern over climate change is driving the development of a fourth generation fluorocarbon, one that meets the requirements of both ozone depletion and climate change regulations, current and anticipated. Honeywell, formerly AlliedSignal, has been the leader in the development of fluorocarbon blowing agents and is now leading the development of this fourth-generation fluorocarbon technology. Honeywell has developed two such fourth generation products: 1234ze(E), a gaseous blowing agent; and a proprietary liquid blowing agent called HBA-2. Both these products successfully incorporate required environmental properties, while maintaining the non-flammability, anticipated non-VOC, and high performance characteristics that have differentiated fluorocarbon blowing agents as the best choice for high performance rigid foam insulation applications. These two fourth generation blowing agents are also ideal for those applications where a flammable blowing agent is unsafe, too costly to use, or fails to provide the desired foam performance. These new high performance materials, while they contain fluorine, also contain an olefin structure, and are therefore referred to as haloalkenes. Because of the presence of a double bond in the molecule backbone, these haloalkenes are a separate and distinct class of materials from their predecessor HFC materials, resulting in a much shorter atmospheric lifetime than their predecessor fluorocarbons, thereby resulting in a much lower GWP.

ENVIRONMENTAL AND REGULATORY UPDATE

Although current activity is limited, the United States government is considering various approaches to address climate change, particularly regulatory-driven changes which, while still too early to predict the final structure and language, will in all probability impact high global warming potential materials to some degree. In anticipation of these regulations and in response to similar regulatory initiatives globally, industry is preparing solutions to meet current and future climate change regulations. Honeywell counts among this group of industries with its low GWP development program, including, in addition to blowing agents, refrigerant gases and other fluorochemicals.

The European Parliament and the Council of the European Union have committed the Community and its Member States adoption of the Kyoto Protocol in reducing anthropogenic emissions of greenhouse gases listed in Annex A to the Kyoto Protocol by 8% compared to 1990 levels in the period from 2008 to 2012.

To this end, the F-Gas Regulation as outlined in (EC) No 842/2006 (OJEC L161 of 14.06.2006) prohibits the use of fluorinated greenhouse gases with a 100-year GWP of 150 or greater, which include certain HFCs (hydrofluorocarbons), PFCs (perfluorocarbons), and SF6 (sulfur hexafluoride) as listed in Annex I (EC 842/2006). The EU F-Gas Regulation will be reviewed in 2011, which may result in additional use restrictions for high GWP fluids (Article 10, F-Gas Regulation).

Honeywell's 1234ze(E) and HBA-2 can provide a substantial in greenhouse gas emission reduction when used in place of high GWP F-gases currently regulated under the EU F-Gas regulation. Since the purpose and intent of the EU F-Gas Regulation is to control emissions of high GWP materials, 1234ze(E), with a GWP of 6, and HBA-2, with a GWP of 7, are in the same GWP range as many other blowing agents that are considered low GWP solutions, such as hydrocarbons. Therefore, these materials provide a path to solving the global warming potential issues facing the industry.

Japan has made voluntary Kyoto Protocol commitments to reduce or limit emissions of greenhouse gases, though has not formally promulgated domestic regulations to enforce these commitments. 1234ze(E) and HBA-2 can play an important role in meeting these voluntary commitments.

It is anticipated that, as climate change regulations are developed in other countries, these regulations will contain similar GWP limits that are being promulgated in Europe and, voluntarily, in Japan. 1234ze(E) and HBA-2 will, in all likelihood, meet or exceed the requirements of these regulations and will therefore be an integral part of any GWP reduction strategy.

Low GWP materials, because of their very short atmospheric lifetime, often prove to be volatile organic compounds (VOCs), contributing to ground level ozone formation. The measure that characterizes whether a chemical is a VOC is the Maximum Incremental Reactivity (MIR). This measure (MIR) at which chemicals are generally considered to be a VOC, by US regulation, is that of ethane. The MIR of both 1234ze(E) and HBA-2 has been measured at less than the value for ethane, hence are expected to be classified as VOC-exempt in the U.S. (Carter, W. P L., 2009). The European Union uses a somewhat different measure to characterize propensity for ground level ozone formation -- photochemical ozone creation potential (POCP) which is reported, and compared to ethane, which has a POCP of 12.3 (Nielsen, University of Copenhagen). 1234ze(E) has a measured POCP of 6.4, well below that of ethane. The POCP of HBA-2 is also estimated to be in this range which means that both these molecules should be considered Low Impact VOCs.

PRODUCT REGISTRATIONS

In the United States, commercialization of new materials requires U. S. Environmental Protection Agency (EPA) compliance with Section 612 of the Clean Air Act (CAA). Toxicology data is submitted to the EPA, together with an application for a Pre Manufacturing Notification (PMN). Approval of the PMN, includes the material’s listing on the Toxic Substances Control Act (TSCA) inventory. Further, materials to be used as blowing agents or in certain other applications must have listing as an acceptable substitute for ozone depleting substances under the Significant New Alternatives Program (SNAP). PMN approval and listing on the TSCA inventory is a requirement for all new chemical materials. SNAP listing is a requirement for all materials in applications that have historically used chlorofluorocarbons (CFC). Upon completion of these regulatory requirements, new materials can be commercialized in the United States. Additionally, these materials may be regulated at the federal, state, or local levels to comply with volatile organic compound (VOC) regulations. 1234ze(E) has completed both the PMN and SNAP process and is now approved for commercial sale in the United States. For, HBA-2, filing for SNAP and PMN has been completed and is currently under U.S. EPA review.

In the European Union, REACH [Registration, Evaluation, Authorization and Restriction of Chemicals, (EC) 1907/2006] regulation has, effective June 1, 2008, replaced the notification provisions of directive 67/548/EEC. Under REACH, each manufacturer or importer of a substance over 1 metric ton per year is obliged to submit a registration file, including a chemical safety assessment for volumes greater than 10 tons. For volumes over 100 and 1000 metric tons, additional data must be submitted. Moreover, for these volume bands, the registrant must submit proposals for animal tests needed to obtain certain (eco) toxicological data points. The goal of the latter provision is to prevent, as much as possible, (duplication of) animal tests. In many cases, waivers for such tests can be proposed. The registration should indicate the intended uses for which the substance is notified. Use outside these registered uses is prohibited, unless a downstream user submits a separate registration file for that use. 1234ze(E) has been notified under REACH at the >1,000 metric ton level. REACH Registration of HBA-2 is in progress.

For Japan, the requirements for commercialization of new chemicals requires submission of toxicological and environmental data to the Japanese Ministry of Health, Labor and Welfare (MHLW), the Ministry of Economy, Trade and Industry (METI), and the Ministry of the Environment (ME) for compliance with the Chemical Substances Control Law. 1234ze(E) and HBA-2 registration in Japan is complete, allowing for commercial sales in Japan.

Other regions of the world, individually, have requirements for toxicology assessment and environmental impact assessment prior to commercialization of new materials. Honeywell is committed to obtaining the necessary regulatory clearances for sampling and eventual sales of both 1234ze(E) and HBA-2 globally. This registration process is in progress for both 1234ze(E) and HBA-2 in several countries, including China, South Korea, Australia, Canada, and others.

TOXICITY

The toxicity testing of both 1234ze(E) and HBA-2 is substantially completed, providing the necessary data for risk assessment for use and commercialization as required by the U.S EPA SNAP and PMN submissions, as well as the EU notification level and other registrations discussed earlier

PROPERTIES

Table 1 and Table 2 list the properties of several low GWP blowing agents compared to HFC-245fa and other commonly used blowing agents. Note that HBA-2 blowing agent exhibits certain key physical properties, such as boiling point and flammability, similar to HFC-245fa and superior to those of cyclopentane. Note that the global warming potential (GWP) of HBA-2 of 7 is more than two orders of magnitude lower than that of currently utilized HFCs, and is more than one order of magnitude lower than the present limitations in the EU F-Gas Regulation. 1234ze(E) has properties more similar to the gaseous blowing agents, specifically HFC-134a. Like HBA-2, the GWP of 1234ze(E) of 6 is more than two orders of magnitude lower than that of HFC-134a at 1430.

Table 1. Liquid Blowing Agent Comparative Properties

Properties	**HBA-2**	**245fa**	**C-C5**	**141b**
Mol. Weight	<134	134	70	117
Boiling Point				
°C	245fa < T_b < 141b	15.3	49.3	32.0
°F	245fa < T_b < 141b	59.5	120.7	89.6
Flashpoint				
°C	None	None	-7.0	None
°F	None	None	19.0	None
LFL/UFL (Vol% in Air)	None	None	1.5-8.7	7.6-17.7
GWP, 100yr[1]	7	1030	11[2]	725
PEL[3]	ND	300	600	500

1. 2007 Technical Summary. Climate Change 2007: They Physical Science Basis. Contribution of Working Group 1 to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. (except where noted)
2. Generally accepted value
3. Manufacturers' literature expect where noted

Table 2. Gaseous Blowing Agent Comparative Properties

Properties	**1234ze(E)**	**134a**	**22**	**142b**
Mol. Weight	114	102	86.5	100.5
Boiling Point				
°C	-19.0	-26.3	-40.8	-9.8
°F	-2.2	-15.3	-41.4	14.4
Flashpoint				
°C	None	None	None	None
°F	None	None	None	None
LFL/UFL (Vol% in Air)	None	None	None	8.0-15.4
GWP, 100yr[1]	6	1430	1810	2310
PEL[3]	1000	1000	1000	1000

1. 2007 Technical Summary. Climate Change 2007: They Physical Science Basis. Contribution of Working Group 1 to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. (except where noted)
2. Generally accepted value
3. Manufacturers' literature expect where noted

Beyond the excellent insulation performance that 1234ze(E) and HBA-2 imparts to polyurethane foam, they are distinctly different from hydrocarbon blowing agents in flammability characterization. 1234ze(E) and HBA-2 shipment, storage, handling, and processing do not require flammability risk mitigation, as is the case with flammable blowing agents such as cyclopentane. 1234ze(E) and HBA-2 are nonflammable by ASTM E-861 test method and have no limitation on hazards classification. 1234ze(E) and HBA-2 are further distinguished from cyclopentane and other hydrocarbon blowing agents by the low potential to contribute to ground level smog formation, and are anticipated to be classified as a non-volatile organic compounds (VOC). Flammability and VOC mitigation may contribute significantly to the OEM's cost of adoption and use and in some cases, such as spray foam, prohibit their use due to safety considerations.

DISCONTINUOUS PANEL FOAM EVALUATIONS

HBA-2 & HBA-2/Cyclopentane Blends - Honeywell Evaluations

Previously, Honeywell has presented an evaluation of physical and thermal properties of HBA-2 against 245fa in a generic polyurethane foam formulation with polyols that were commonly used in North America. Honeywell, being a global company, conducted a similar study using a generic formulation with polyols that can be easily acquired in China. The thermal conductivity, reactivity, dimensional stability, compressive strength and flammability of polyurethane foams with HBA-2 were compared against those third generation liquid blowing agents, such as 245fa and cyclopentane, and a second generation liquid blowing agent, 141b, which are commercially available in China. Furthermore, properties of foams with various HBA-2/cyclopentane blends were also evaluated aiming to seek a balance between superior foam properties and desired cost.

The compositions of a generic formulation with various blowing agents are listed in Table 3. This generic polyurethane foam formulation utilized was developed to yield a free rise density of about 1.9 lb/ft^3. With approximately 20% overpacking, the density of the prepared foams ranged from 2.2 lb/ft^3 to 2.3 lb/ft^3. All the foams were prepared by a hand-mixing method with processing conditions given in Table 4. The blended foam was poured into a mold at 104°F and allowed to cure for 30 minutes before demolding. All physical property and thermal conductivity testing were performed at least 24 hours after foams were prepared.

Note that this experiment is considered as a "drop-in" replacement study to determine the blowing agent feasibility. The generic polyurethane foam formulation used in this study was developed using 245fa as blowing agent. The formulation used in this evaluation is not optimized for other blowing agents.

Table 3. Generic Formulation of Discontinuous Panel Foam Evaluated

Components	**HBA-2**	**245fa**	**C-C5**	**141b**
Polyether Polyol	65.0	65.0	65.0	65.0
Polyester Polyol	35.0	35.0	35.0	35.0
Catalysts	2.0	2.0	2.0	2.0
Surfactant	1.5	1.5	1.5	1.5
Flame Retardant	22.0	22.0	22.0	22.0
Water	2.0	2.0	2.0	2.0
Blowing Agent	Equal-Molar	24.0	12.5	20.9
Isocyanate, Index = 110	143.6	143.6	143.6	143.6

Table 4. Hand-Mixing Method – Preparation Parameters and Conditions	
Parameters	**Conditions**
Component Temperature	
Polyol Premix	68°F/20°C
Isocyanate	68°F/20°C
Stirring	
Speed	5000 RPM
Duration	5 seconds
Mold Dimensions	4”x12”x12” / 10cm x 30cm x 30cm
Mold Temperature	104°F/40°C

Table 5. Densities of Foams with Various Blowing agents and Blowing Agent Blends					
Physical Properties	**HBA-2**	**245fa**	**C-C5**	**141b**	
Free Rise Density, lb/ft^3	1.83	1.77	1.85	1.92	
Free Rise Density, kg/m^3	29.3	28.3	29.7	29.8	
Core Density, lb/ft^3	2.35	2.29	2.31	2.32	
Core Density, kg/m^3	37.6	36.7	37.1	37.2	
	HBA-2/Cyclopentane mol% Ratio				
Physical Properties	**100/0**	**75/25**	**50/50**	**25/75**	**0/100**
Free Rise Density, lb/ft^3	1.83	1.83	1.79	1.71	1.85
Free Rise Density, kg/m^3	29.3	29.3	28.6	27.3	29.7
Core Density, lb/ft^3	2.35	2.33	2.33	2.37	2.35
Core Density, kg/m^3	37.6	37.4	37.4	38.0	37.7

When compared the free rise density and core density of the polyurethane foams prepared with blowing agents or blowing agent blends, they are within 10% range of each other in Table 5. Since prepared foams have essentially identical density, comparisons of their physical, thermal properties are considered as fair and valid.

Table 6A.Foam Reactivity and Properties with Various Blowing Agents				
Foam Reactivity	**HBA-2**	**245fa**	**C-C5**	**141b**
Gel Time, sec	55	55	52	52
Tack Free Time, sec	100	100	95	95
Dimensional Stability, ΔVol %[1]	**HBA-2**	**245fa**	**C-C5**	**141b**
-29°C, Aged 28 Days	-1.21	-1.75	-1.13	-1.61
90°C, Aged 28 Days	3.14	3.86	7.67	9.62
70°C/95%RH, Aged 28 Days	3.83	3.98	6.42	14.96
Compressive Strength[2]	**HBA-2**	**245fa**	**C-C5**	**141b**
Parallel, psi	40.2	41.3	36.2	38.9
Parallel, kPa	277.5	284.5	249.9	268.0
Perpendicular, psi	27.2	28.8	24.0	27.7
Perpendicular, kPa	187.5	198.5	165.2	190.7

[1] Dimensional stability of foam was evaluated as per ASTM D-2126-04
[2] Compressive strength of foam was evaluated as per ASTM D-1621

As shown in Table 6A, foams with HBA-2 demonstrate reactivity and physical properties comparable to those with 245fa. Furthermore, they demonstrate significantly better dimensional stability at high temperatures than those with cyclopentane or 141b, and considerably higher compressive strength that those with cyclopentane.

Table 6B. Foam Reactivity and Properties with Various Blowing Agents Blends					
	HBA-2/Cyclopentane mol% Ratio				
Physical Properties	**100/0**	**75/25**	**50/50**	**25/75**	**0/100**
Gel Time, sec	55	54	53	52	52
Tack Free Time, sec	100	99	95	85	100
Dimensional Stability, ΔVol %[1]	**100/0**	**75/25**	**50/50**	**25/75**	**0/100**
-29°C, Aged 28 Days	-1.21	-1.15	-1.53	-2.15	-1.13
90°C, Aged 28 Days	3.14	4.66	5.03	3.44	7.67
70°C/95%RH, Aged 28 Days	3.83	3.40	5.93	5.58	6.42
Compressive Strength[2]	**100/0**	**75/25**	**50/50**	**25/75**	**0/100**
Parallel, psi	40.2	40.0	35.0	35.8	36.2
Parallel, kPa	277.5	275.8	241.6	247.0	249.9
Perpendicular, psi	27.2	26.1	24.9	28.4	24.0
Perpendicular, kPa	187.5	180.0	171.4	195.8	165.2

[1] Dimensional stability of foam was evaluated as per ASTM D-2126-04
[2] Compressive strength of foam was evaluated as per ASTM D-1621

Referring to Table 6B, blending HBA-2 with cyclopentane appears to enhance various physical properties when compared to foams with only cyclopentane. For instance, at high temperature conditions, such as 90°C and 70°C/95%RH, the dimensional stability is improved as the concentration of HBA-2 increased in the blend. Also, it is important to stress that foams with 75/25mol% HBA-2/cyclopentane provides almost identical foam reactivity and similar superior physical properties to foams blown with HBA-2 alone. However, mixtures of cyclopentane and HBA-2 are considered as flammable which probably require explosion-proof equipment for processing.

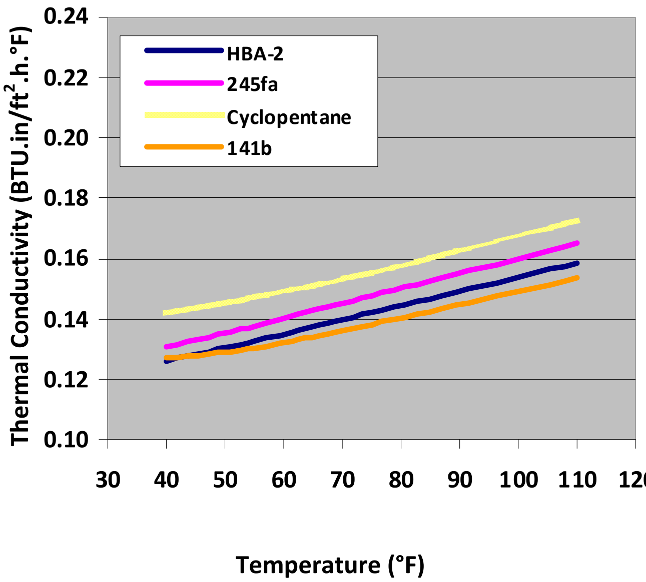


Figure 1. Initial Thermal Conductivity of Foams with Various Blowing Agents

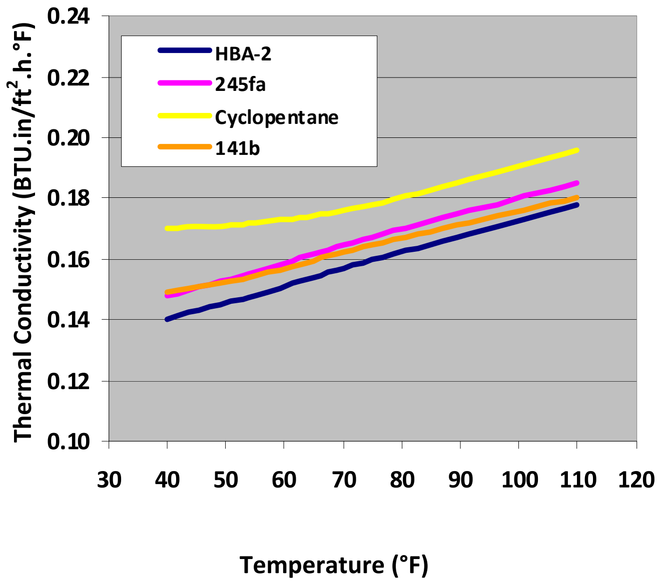


Figure 2. Thermal Conductivity of Foams with Various Blowing Agents after 28 Days

Figure 1 and Figure 2 show the initial and 28-day aged thermal conductivity of foams with various blowing agents respectively. Foams containing HBA-2 provide better thermal insulation value, approximately 4% lower initial thermal conductivity, than those with 245fa at all evaluated mean temperatures, 40°F/4°C, 55°F/13°C, 70°F/21°C and 110°F/43°C. A similar phenomenon was also noted after 28 days aging at room temperature but by a wider margin, about 6% between those curves. This suggests that foams with HBA-2 retained its thermal insulation value better than their counterparts with 245fa. Honeywell has previously reported similar results in 2010 when a U.S. generic formulation was evaluated.[2] Although foams with 141b appear to have better thermal insulation value than those with HBA-2 at higher temperatures, the trend begins to show a reverse behavior at approximately 45°F/7°C and lower, which falls into the operating temperature range of pour-in-place applications, such as walk-in freezers and cold storage. Furthermore, after 28 days of aging, foams with HBA-2 demonstrate considerably better thermal insulation value than all blowing agents, including 141b, at all evaluated temperatures. The thermal conductivity of foams with cyclopentane is the highest among all tested samples regardless of evaluated temperatures and aging durations. Furthermore, the thermal conductivity of foams with cyclopentane begins to level off when the evaluated temperatures are below approximately 75°F, reducing its effectiveness in cold storage applications, such as coolers and freezers that require foams with superior thermal insulation value at 20°F and 55°F correspondingly.

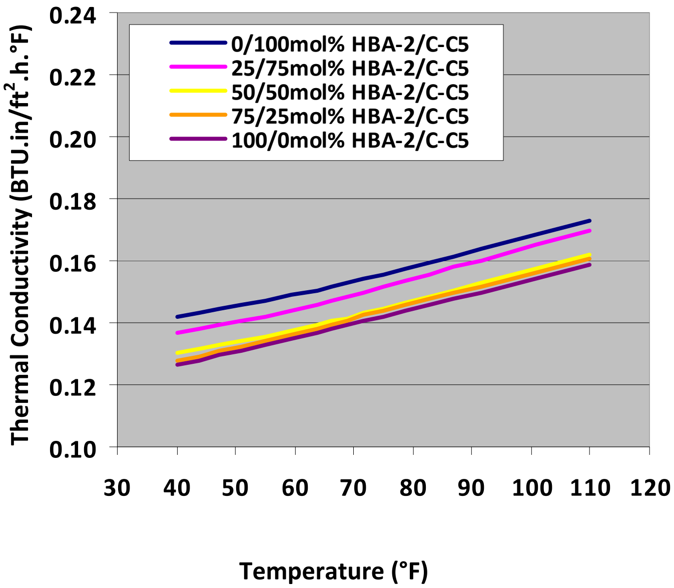


Figure 3. Initial Thermal Conductivity of Foams with Various Blowing Agent Blends

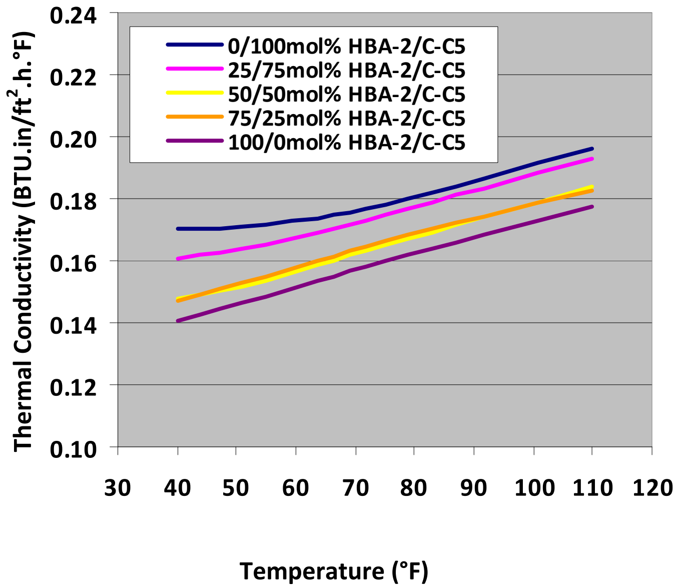


Figure 4. Thermal Conductivity of Foams with Various Blowing Agent Blends after 28 Days

According to Figure 3, although the thermal insulation value of foams deteriorates as the percentage of cyclopentane in the blend increases, the trend does not appear to be linear. Blending of up to 50 mol% of cyclopentane with HBA-2 demonstrates no significant impact on initial thermal conductivity throughout the temperatures evaluated. This is particular beneficial to pour-in-place applications which are looking for foam with a balance of superior thermal properties and acceptable cost of blowing agent. As illustrated in Figure 4, the aged thermal conductivity of foams with a composition equal to or higher than 75mol% cyclopentane appears to have a more noticeable plateau effect than the others. This phenomenon may not be favorable to cold chain application due to its low operation temperatures. Although certain HBA-2/cyclopentane blends may be able to provide a desired balance between properties and cost, foams with HBA-2 are still the best with respect to both initial and aged thermal insulation values. Also note that the HBA-2 foams retain their k-factor better than any of the blends evaluated.

Table 7. Measured Flame Height of Foam Samples During the Flammability Test

B2 Test Evaluation[1]	HBA-2	245fa	141b	C-C5
Flame Height, cm	10.0	12.0	12.0	15.0

	HBA-2/Cyclopentane mol% Ratio				
B2 Test Evaluation[1]	**100/0**	**75/25**	**50/50**	**25/75**	**0/100**
Flame Height, cm	10.0	11.0	12.0	13.0	15.0

[1] Flammability of foams was evaluated as per DIN 4102-1: Class B2 Materials

All foams were evaluated for flammability performance using the DIN 4102 B2 test method. In order to pass the DIN 4102-1: Class B2 material evaluation, the flame height could not surpass the gauge which located 15cm above the ignition point during the first 15 seconds of the test. According to Table 7, Foams with HBA-2 has the best flame retardancy when compared to those with 245fa, 141b or cyclopentane. Foams with cyclopentane only passed the evaluation marginally. For the blends, as the concentration of cyclopentane increases, the flame retardancy decreases.

1234ze(E)/Cyclopentane Blends - Honeywell Evaluations

In this study, a generic polyurethane foam formulation similar to that listed in Table 3 but with polyols that can be acquired in the U.S. was employed to evaluate properties of foams with various compositions of 1234ze(E)/cyclopentane blends through equal molar substitutions of blowing agents in the formulation. Foams with core density between 2.1lb/ft^3 - 2.2lb/ft^3 were prepared by using a high pressure Edge-Sweets machine.

As shown in Figure 5, the initial thermal conductivity generally increases as the loadings of cyclopentane decreases. The differences in initial thermal conductivity of these blends become more apparent as the evaluated temperature increases. For instance, the thermal conductivity of foams with only cyclopentane and with 87/13mol% of cyclopentane/1234ze(E) appears to have no significant difference under 40°F but not above 75°F. As the foams aged, the thermal insulation value at lower temperatures appears to deteriorate faster. However, blending 1234ze(E) with cyclopentane appears to reduce this deterioration rate. For example, foams with 87/13mol% of cyclopentane/1234ze(E) blend provide notably lower thermal conductivity than those with cyclopentane alone. Since the use of 1234ze(E) lessens the nonlinearity of the relationship between thermal conductivity and temperature that is common for foams with cyclopentane, the use of these blends may be useful in certain cyclopentane foams that may need low temperature performance improvement.

Table 8. Physical Properties of Foams with Various Blowing Agent Blends

	Cyclopentane/1234ze(E) mol% Ratio		
Dimensional Stability, ΔVol %[1]	**100/0**	**87/13**	**75/25**
-29°C, Aged 28 Days	0.1	0.1	-0.2
90°C, Aged 28 Days	9.8	6.1	1.2
70°C/95%RH, Aged 28 Days	13.5	11.8	3.4
Compressive Strength[2]	**100/0**	**87/13**	**75/25**
Parallel, psi	23.0	21.0	19.7
Parallel, kPa	158.6	144.8	135.8
Perpendicular, psi	19.8	17.0	17.8
Perpendicular, kPa	136.5	117.2	122.7

[1] Dimensional stability of foam was evaluated as per ASTM D-2126-04
[2] Compressive strength of foam was evaluated as per ASTM D-1621

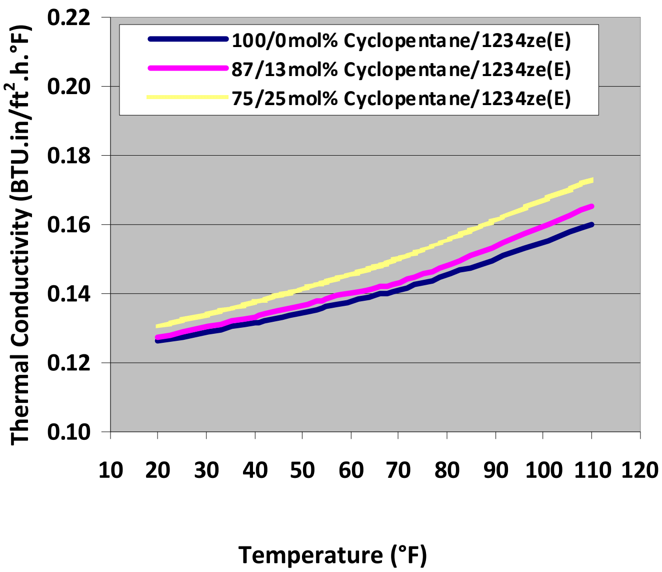


Figure 5. Initial Thermal Conductivity of Foams with Various Blowing Agent Blends

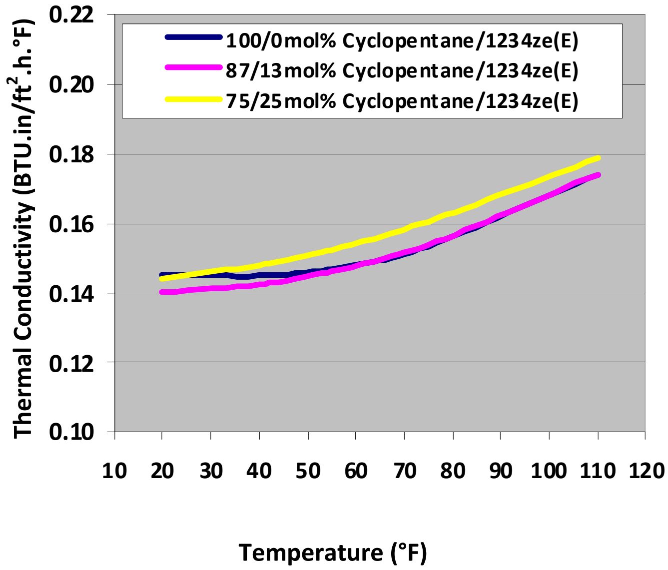


Figure 6. Thermal Conductivity of Foams with Various Blowing Agent Blends after 28 Days

Blending up to 25mol% of 1234ze(E) with cyclopentane has minor impact on both parallel and perpendicular compressive strength. However, the data indicated that there is an improvement of foams' dimensional stability at both ambient and humid hot conditions as the concentration of 1234ze(E) increases in Table 8.

Table 9. Measured Flame Height of Foam Samples During the Flammability Test

	Cyclopentane/1234ze(E) mol% Ratio			
B2 Test Evaluation[1]	**100/0**	**87/13**	**75/25**	**0/100**[2]
Flame Height, cm	14.0	13.3	12.7	7.5

[1] Flammability of foams was evaluated as per DIN 4102-1: Class B2 Materials
[2] Foams with about 15% higher density than the rest, included as comparison purposes only

In order to pass the DIN 4102-1: Class B2 material evaluation, the flame height could not surpass the gauge which is located 15cm above the ignition point during the first 15 seconds of the test. Although all the foam samples prepared with different compositions of cyclopentane/1234ze(E) passed the flammability test, the flame retardancy of foams with 100mol% of cyclopentane are the worst while those with 100mol% 1234ze(E) are the best. Blending 1234ze(E) with cyclopentane appears to enhance flame retardancy of foam as indicated by the flame height results of foams with 87/13mol% and 75/25mol% cyclopentane/1234ze(E) blends correspondingly, as shown in Table 9.

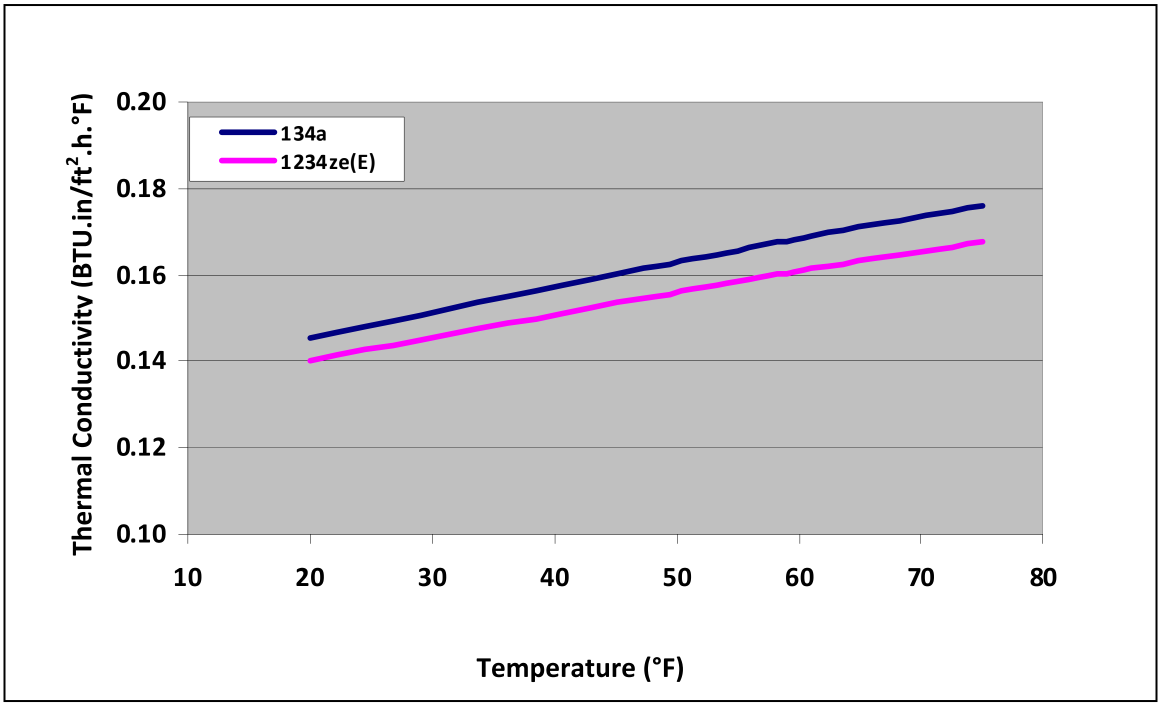
1234ze(E) Evaluation - System House Evaluation

A polyurethane foam system house has performed a near "drop-in" evaluation of the LGWP gaseous blowing agent, 1234ze(E), in a 134a commercial polyurethane foam formulation except the blowing agent loading was adjusted for the blowing agent's molecular weight. This froth formulation was prepared with the component temperatures at 88°F/31°C and a polyol/isocyanate mix ratio of 110 to 100. The reactivity and physical properties of foams with 1234ze(E) and the 134a control are listed in Table 10 for comparison.

Table 10. Reactivity and Physical Properties of Foams with Gaseous Blowing Agents

Foam Density	**1234ze(E)**	**134a**
Free Rise Density, lb/ft^3	1.79	1.65
Free Rise Density, kg/m^3	28.7	26.4
Core Density, lb/ft^3	2.11	2.00
Core Density, kg/m^3	33.8	32.0
Foam Reactivity	**1234ze(E)**	**134a**
Cream Time, sec	Froth	Froth
Gel Time, sec	71	120
Tack Free Time, sec	112	185
Physical Strength	**1234ze(E)**	**134a**
Compressive Strength, psi	21.0	21.0
Compressive Strength, kPa	144.8	144.8
Shear Strength, psi	38.0	41.0
Shear Strength, kPa	262.0	282.7
Flexural Strength, psi	41.0	31.0
Flexural Strength, kPa	282.7	213.7
Dimensional Stability, ΔVol %	**1234ze(E)**	**134a**
200°F/93°C, 28 days	0.15	7.20
158°F/70°C, 95% RH, 28 days	2.14	-1.90
-20°F/-29°C, 28 days	0.38	-1.10
Closed Cell Content, %	**1234ze(E)**	**134a**
Closed Cell Content	> 90	> 90

As per the results shown in Table 10, this near "drop-in" formulation with 1234ze(E) provides similar foam densities, comparable physical strengths and equal closed cell content as the 134a benchmark. Furthermore, the dimensional stability of foams at both 200°F/93°C and -20°F/-29°C appears to be noticeably better with 1234ze(E). Most importantly, foams with 1234ze(E) provides about 5% better initial thermal insulation properties than those with 134a control at all the temperature evaluated as shown in Figure 7.



COMMERCIALIZATION STATUS

Honeywell has successfully commercialized 1234ze(E) in the EU in several foam applications coinciding with the implementation of the EU F-Gas Regulation constraints on the use of high GWP materials. Commercialization of 1234ze(E) in Japan and the U.S. is well underway with several successful major customer trials completed and additional trials planned. 1234ze(E) has been available commercially since 2008, and Honeywell recently announced that it will build a commercial scale plant in Baton Rouge, expected to startup in 2013. HBA-2 is expected to be commercial in late 2012/2013

With respect to U.S. commercialization of 1234ze(E), the Environmental Protection Agency's SNAP office has added 1234ze(E) to the list of acceptable substitutes for ozone-depleting substances in certain foam, refrigerant, aerosol, and sterilant gas applications. That notice appeared in the Federal Register/Vol. 74/No. 188 on Wednesday, September 30, 2009 (p. 50132) and Federal Register/Vol.75/No.115 on Wednesday, June 16, 2010 (p. 34039 ff). 1234ze(E) PMN (Pre Manufacturing Notification) has been approved by the U.S. EPA. Because of these EPA actions, 1234ze(E) is now allowed for commercial use in certain applications. In the EU, HBA-2 is in the process of REACH registration, and has been approved for commercial sales in Japan under the Japan Chemical Substances Control Law. In the U.S., Honeywell has completed HBA-2 SNAP and PMN filings and the U.S. EPA is currently reviewing these filings. Development is well underway and on tracks with major successful customer trials completed or underway in all major applications.

CONCLUSIONS

Honeywell fourth generation LGWP liquid blowing agent, HBA-2, and gaseous blowing agent, 1234ze(E), demonstrated superior thermal properties and comparable physical properties compared to their third generation counterparts, 245fa and 134a, through in-house generic formulation and system house's commercial formulation correspondingly. HBA-2 further demonstrated better overall foam properties which surpass those of cyclopentane, and a second generation blowing agent, 141b. Blends of cyclopentane with either Honeywell LGWP blowing agents provide viable options that can balance cost with the need to fulfill physical properties and thermal insulation requirements for different insulated metal panel applications; in particular those require superior thermal insulation value at low temperature. Honeywell LGWP molecules, 1234ze(E) and HBA-2, and the blends with cyclopentane has proved to provide LGWP blowing agent solutions for pour-in-place applications.

REFERENCES

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BIOGRAPHY

Jim Y.K. Ling

Jim holds a B.A.Sc degree and an M.Eng degree in Chemical Engineering and Applied Chemistry from University of Toronto, Canada and is a registered Professional Engineer under PEO in the province of Ontario, Canada. He worked as a research and development scientist for ShawCor Ltd. in the spray applied rigid polyurethane foam sector for thermal insulation applications. Jim joined Honeywell in 2007 and is currently a global technology sector leader in the blowing agent technical service and development group with primary responsibility for pour-in-place foam applications of fluorocarbon products.

Ryan S.L. Qin

Ryan possesses a B.S. degree in polymer science and engineering from East China University of Science and Technology and a M.S. degree in Material Science from Fudan University. He worked as a research and development scientist for BASF Polyurethane Specialty Co. Ltd in the construction insulation applications. Ryan joined Honeywell in 2009. His responsibilities include application developments, technical services and new product developments for fluorocarbon blowing agents in appliance, spray, panel and commercial cold storage industries in China and other Asia-Pacific Regions.