Evaluation of HBA-2, a Low GWP Blowing Agent, in Pour-in-place Panel Applications

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ABSTRACT

Honeywell is developing a liquid, low global warming potential (LGWP), non-flammable blowing agent, HBA-2, for rigid polyurethane foam applications. In this paper, a laboratory evaluation of HBA-2, including miscibility in various polyols commonly used in pour-in-place panel foams, and a comparison of physical properties of pour-in-place panel foams with commercially available blowing agents and HBA-2 is provided.

INTRODUCTION

Polyurethane foam is used extensively as the core insulation material in metal panels in many applications, including the walk-in cooler and freezer sectors. These foam core metal panels can be manufactured by either continuous or discontinuous production methods. In the construction industry, they are employed as insulation in the building envelope of commercial structures. In developed countries, the most commonly used blowing agents for polyurethane foam in this application include 245fa, 134a and hydrocarbons. In contrast, 141b is still used as the blowing agent in the majority of the polyurethane foam markets in developing countries. As the low global warming potential initiative emerges in developed countries and the HCFC phase-out in developing countries approaches, manufacturers' interest in the next generation, low global warming potential (LGWP) blowing agents is growing worldwide.

In this paper, the physical, flammability and environmental properties of various commercially available blowing agents are compared. Furthermore, comparisons of Honeywell's HBA-2 and 245fa blowing agents on polyol miscibility and on the thermal conductivity and physical properties of foams prepared are included.

PHYSICAL PROPERTIES

To address potential global warming regulations, various chemicals are currently being evaluated to be used as blowing agents to replace HFCs, such as 245fa, 365mfc and 134a. Honeywell has developed a liquid, low global warming potential (LGWP), non-flammable blowing agent, HBA-2, for the rigid polyurethane foam industry. Table 1 provides a comparison of the physical properties of HBA-2 and other commonly used blowing agents, such as 245fa, cyclopentane and 141b. Compared to 245fa, HBA-2 has a higher boiling point and lower molecular weight. Hence, the storage and handling procedures of HBA-2 should be easier compared to 245fa. Furthermore, the usage level by weight of blowing agent in the formulation will be less than that for 245fa. Most importantly, the loss of blowing agent from the polyol system, in particular during blending and during shipping in drums, should be decreased because the vapor pressure of HBA-2 is lower than that of 245fa.

Table 1. Physical Properties of Blowing Agents

Physical Properties	**HBA-2**	**245fa**	**Cyclopentane**	**141b**
Formula	-	$CF_3CH_2CF_2H$	C_5H_{10}	CH_3CCl_2F
Molecular Weight, g/mol	< 245fa	134.0	70.0	116.9
Boiling Point, °C/°F	> 245fa < 141b	15.3 / 59.5	49.3 / 120.7	32.2 /90.0
Liquid Density, g/cc @20°C/68°F	1.30	1.32	0.74	1.24
Vapor Pressure, kPa @20°C/68°F	106.3	122.0	34.0	69.0
Vapor Thermal Conductivity, mW/mK @10°C[1]/50°F	12.5[1]	12.5[2]	11	8.8

[1] Honeywell measured value
[2] Property was measured at 24°C

ENVIRONMENTAL PROPERTIES

HBA-2 is a liquid blowing agent with low global warming potential. Table 2 summarizes the environmental properties of HBA-2 compared to other commonly used blowing agents. Compared to 245fa and 141b, HBA-2 has a significantly lower global warming potential. Furthermore, test data suggest that it will be unlikely that HBA-2 would be considered a volatile organic compound (VOC) in the US and subject to emission controls.

Table 2. Environmental Properties of Blowing Agents

Environmental Properties	HBA-2	245fa	Cyclopentane	141b
GWP (100 yr horizon, CO_2 = 1)[1]	7	1030	11	725
Atmospheric Lifetime	28 days	8.4 yrs	Few Days	9.4 yrs
VOC status	No[2]	No	Yes	No

[1] 245fa and 141b data were obtained from IPCC report "Climate Change 2007 – The Physical Science Basis". Cyclopentane data is a generally accepted value.
[2] Honeywell data shown that HBA-2 is not a VOC, pending EPA approval

FLAMMABILITY PROPERTIES

Similar to 245fa, HBA-2 is classified as a non-flammable liquid blowing agent with neither a flash point nor vapor flame limits in air. Table 3 summarizes the flammability properties of different blowing agents. 141b is classified as combustible with vapor flame limits but no flash point while hydrocarbons, such as cyclopentane, exhibit flash points and are therefore flammable. The use of flammable materials will generally require major capital investment in storage and processing equipment modifications.

Table 3. Flammability Properties of Blowing Agents

Flammability Properties	HBA-2	245fa	Cyclopentane	141b
Vapor Flame Limits in Air Upper, Vol % Lower, Vol %	 None None	 None None	 7.6 17.7	 1.5 8.7
Flashpoint, °C/°F	None	None	-37.0/-34.6	None

TOXICITY ACCESSMENTS

Comprehensive toxicity assessments of new blowing agent molecules are vital before commercialization. The toxicity information directly affects the exposure guidelines during the foam manufacturing process. Furthermore, the information is critical to considerations in product stewardship and responsible care. Toxicity testing results to date indicate that HBA-2 has a very low order of acute toxicity which is either equivalent to or better than that of 245fa. Further assessments, such as long term toxicological data, are nearing completion that will complete the toxicity testing of the molecule.

POLYOL MISCIBILITY EVALUATIONS

In the panel foam industry, it is often necessary to blend a blowing agent into the polyol premix in the manufacturing facility regardless of the production methods, either continuous or discontinuous. Adequate miscibility of blowing agent in polyol is necessary to produce polyurethane foam with desirable physical and thermal properties. A simple evaluation was conducted to compare the miscibility of HBA-2 compared to 245fa in various polyols commonly used in panel foam applications. Table 5 lists the name, type and suppliers of polyols evaluated in this miscibility study.

In this experiment, a mixture of 40 wt% blowing agent and 60 wt% polyol was prepared in a Fischer Porter tube. The tube was then vigorously shaken and thoroughly mixed. The appearance of the mixture was recorded after the tubes were conditioned at room temperature for 24 hours. If a phase separation was detected, the amount of blowing agent dissolved was indirectly calculated by measuring the height of the blowing agent phase which had settled at the bottom of the tube. Table 6 shows the miscibility of HBA-2 and 245fa in the evaluated polyols correspondingly. Furthermore, Figure 1 and Figure 2 show the appearance of the polyol mixture with blowing agent after having been aged at room temperature for 24 hours.

Both HBA-2 and 245fa appear to be more miscible in the polyether polyols than in the polyester polyols evaluated. At least 40 wt% of either blowing agent can be blended into the polyether polyols evaluated without phase separation. All in all, HBA-2 has demonstrated excellent solubility in polyether polyols evaluated and adequate miscibility in polyester polyols tested.

Table 5. Polyols Evaluated in the Miscibility Study

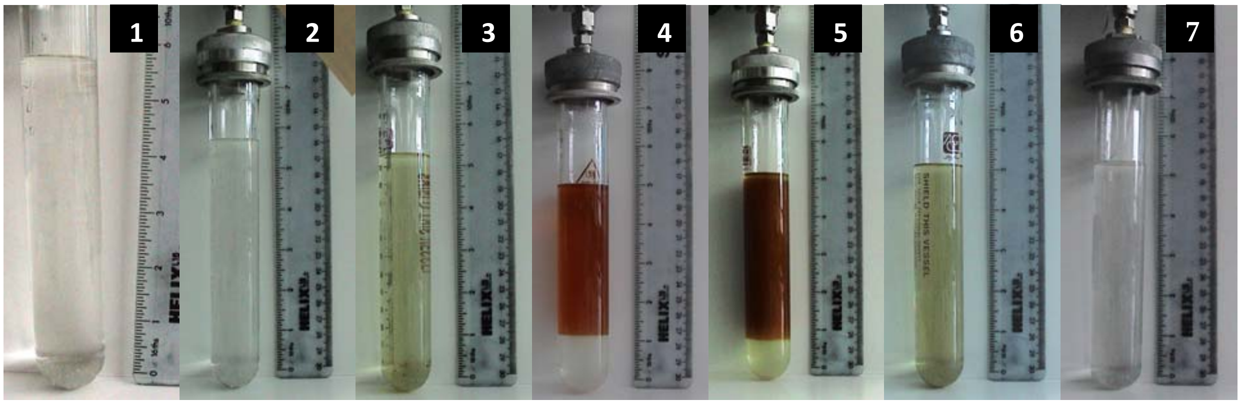
	Polyol Name	Polyol Type
1	Voranol® 270[1]	Glycerine Initiated Polyether Polyol
2	Voranol® 490[1]	Surcose/Glycerine Initiated Polyether Polyol
3	Voranol® 800[1]	Aliphatic-amine initiated Polyether Polyol
4	Terate® 4020[2]	Aromatic Polyester Polyol
5	Terate® 2031[2]	Aromatic Polyester Polyol
6	Carpol® GSP-280[3]	Surcose/Glycerine Initiated Polyether Polyol
7	Multranol® 3901[4]	Polyether Polyol

[1] Registered Trademark of The Dow Chemical Company
[2] Registered Trademark of Invista
[3] Registered Trademark of Carpenter Co.
[4] Registered Trademark of Bayer Corporation

Table 6. Miscibility of 245fa and HBA-2 in Various Polyols

Polyol Name	HBA-2		245fa	
	Phase Separation	Wt% Miscibility	Phase Separation	Wt% Miscibility
Voranol® 270[1]	No	$\geq$ 40	No	$\geq$ 40
Voranol® 490[1]	No	$\geq$ 40	No	$\geq$ 40
Voranol® 800[1]	No	$\geq$ 40	No	$\geq$ 40
Terate® 4020[2]	Yes	~ 20	Yes	~ 18
Terate® 2031[2]	Yes	~ 11	Yes	~ 20
Carpol® GSP-280[3]	No	$\geq$ 40	No	$\geq$ 40
Multranol® 3901[4]	No	$\geq$ 40	No	$\geq$ 40

[1] Trademark of The Dow Chemical Company
[2] Trademark of Invista
[3] Trademark of Carpenter Co.
[4] Trademark of Bayer Corporation



From Left to Right: (1) Voranol 270, (2) Voranol 490, (3) Voranol 800, (4) Terate 4020, (5) Terate 2031, (6) Carpol GSP-280, (7) Multranol 3901

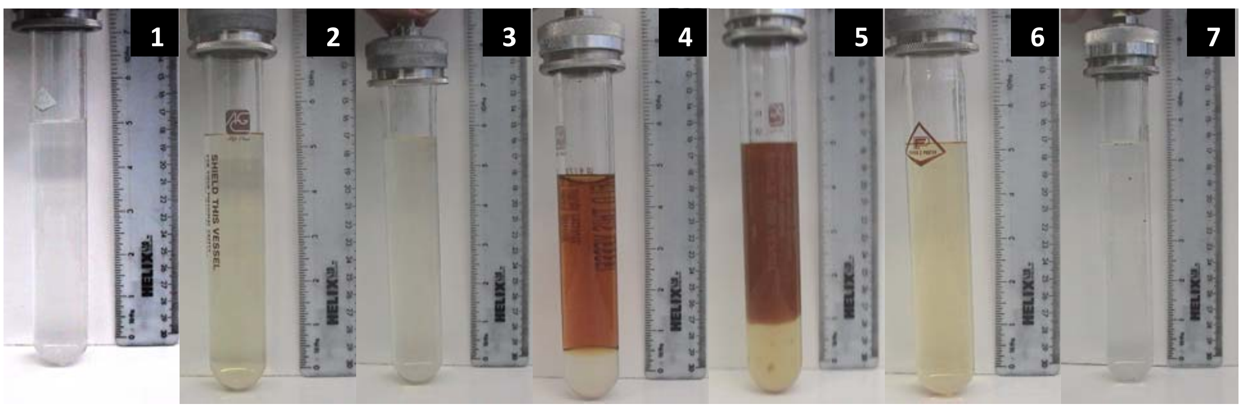


Figure 2. Polyols with HBA-2 in Fischer Porter Tubes
From Left to Right: (1) Voranol 270, (2) Voranol 490, (3) Voranol 800, (4) Terate 4020, (5) Terate 2031, (6) Carpol GSP-280, (7) Multranol 3901

DISCONTINUOUS PANEL FOAM EVALUATIONS

Foam core metal panels are used extensively in many different applications, such as walk-in coolers, walk-in freezer, cold storage and various commercial structures. One of the key performance criteria for metal panels is the R-value, i.e. the reciprocal of thermal conductivity. Therefore, the focus of this study was to compare the thermal conductivity of foams with either 245fa or HBA-2. The physical properties, such as foam reactivity, dimensional stability and compressive strength, were also compared.

The compositions of the generic formulation with different blowing agents are listed in Table 7. The generic panel foam formulation utilized was developed to yield a free rise density of about 1.9 lb/ft^3. Using 20% overpacking, the resultant density of the foams was between 2.2 lb/ft^3 and 2.3 lb/ft^3. All the discontinuous panel foams were prepared by utilizing the Edge-Sweets high pressure foam machine with processing conditions given in Table 8. The foam was shot into a preheated mold, at 120°F to 125°F, and allowed to cure in a 130°F oven for 20 minutes before demolding. All physical property and thermal conductivity testing, was performed at least 24 hours after the foam was prepared.

It is important to emphasize that this experiment is considered as a preliminary “drop-in” replacement study to determine the blowing agent feasibility. The generic discontinuous panel foam formulation used in this study was developed using 245fa as the blowing agent. The formulation used in this evaluation for HBA-2 is not yet considered optimal for this blowing agent.

Table 7. Generic Formulation of Discontinuous Panel Foam Evaluated

Components	HBA-2	245fa
Polyether Polyol	65.0	65.0
Polyester Polyol	35.0	35.0
Catalyst	2.0	2.0
Surfactant	1.5	1.5
Flame Retardant	22.0	22.0
Water	2.0	2.0
Blowing Agent	Equal-molar	24.0
Isocyanate, Index = 110	143.6	143.6

Table 8. Discontinuous Panel Foams’ Preparation Parameters and Conditions

Parameters	**Conditions**
Equipment	Edge-Sweets High Pressure Machine
Machine Pressure	2000 psi / 13.8 MPa
Foam Output	
Flow Output	15 lb/min / 6.8 kg/min
Polyol Temperature	68 - 72°F / 20 - 22°C
Isocyanate Temperature	68 - 72°F / 20 - 22°C
Injection Time, blowing agent dependent	3.0 - 3.1 seconds
Mold Temperature	120°F - 125°F / 48.9°C- 51.7°C
Mold Dimensions	2’ x 1’ x 2” / 30.5cm x 15.3cm x 5.1cm

Table 9. Resultant Foam Density of Discontinuous Panel Foams

Foam Density	**HBA-2**	**245fa**
Free Rise Density, lb/ft^3	1.87	1.86
Free Rise Density, kg/m^3	30.0	29.8
Core Density, lb/ft^3	2.21	2.23
Core Density, kg/m^3	35.2	35.2

The free rise density and core density of the discontinuous panel foams prepared are tabulated in Table 9. The resultant free rise and core foam densities are within 5% range of each other with HBA-2 and 245fa as blowing agents. Because the foams are essentially the same density, a comparison of the physical properties is fair and valid.

THERMAL CONDUCTIVITY

The thermal conductivity of the foams were evaluated at five mean temperatures, 20°F/-7°C, 40°F/4°C, 55°F/13°C, 70°F/21°C and 110°F/43°C. Figure 3 and Figure 4 show the initial and 28-day aged thermal conductivity of the foams respectively. The foams containing HBA-2 provides better thermal insulation value, approximately 5% lower initial thermal conductivity, than those with 245fa at all evaluated temperatures. The difference in thermal conductivity increased to 10% after the foams were aged for 28 days. Compared to foam with 245fa, those with HBA-2 may provide either similar thermal insulation value with thinner foam insulation or offer better energy efficiency at an equal foam thickness.

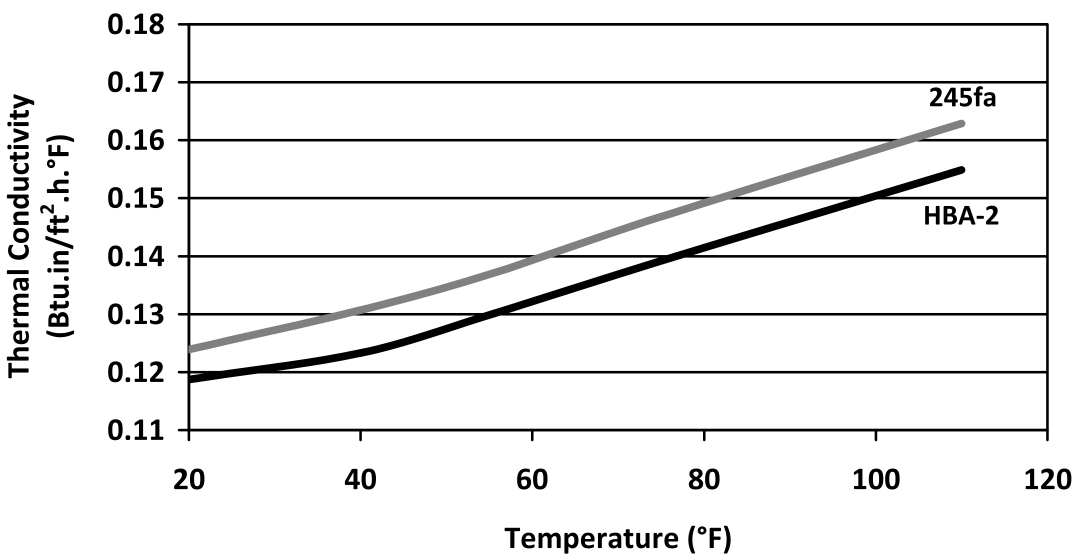


Figure 3. Initial Thermal Conductivity of Foams with Different Blowing Agents

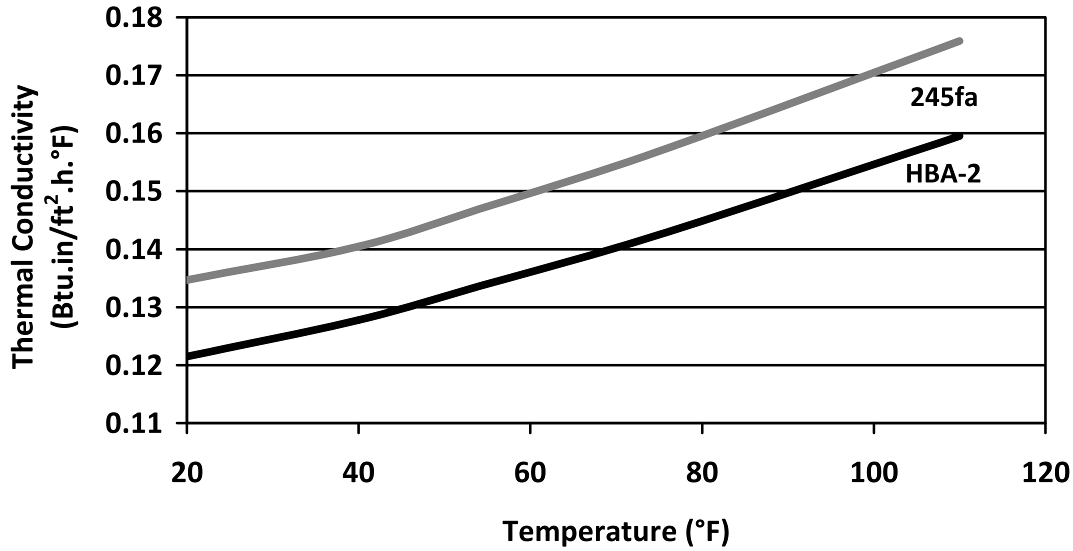


Figure 4. Thermal Conductivity of Foams with Different Blowing Agents after 28 Days Aging at Ambient Temperature

PHYSCIAL PROPERTIES

Foams with HBA-2 blowing agent provide comparable physical properties compared to those foams with 245fa. Table 9 shows the foam reactivity, dimensional stability and compressive strength of both systems. Comparable foam reactivity and dimensional stability were found for both foams. Comparing the parallel and perpendicular compressive strength, the data suggested that foam with HBA-2 has a more isotropic cell structure than that with 245fa.

Table 10. Foam Reactivity and Typical Properties

Foam Reactivity	**HBA-2**	**245fa**
Gel Time, sec	38	40
Tack Free Time, sec	150	127
Dimensional Stability, Vol. % Change[1]	**HBA-2**	**245fa**
Cold, -29°C, Aged 28 Days	-0.69	-0.17
Hot, 90°C, Aged 28 Days	2.60	4.18
Hot & Humid, 70°C/95%RH, Aged 28 Days	8.21	6.66
Compressive Strength[2]	**HBA-2**	**245fa**
Perpendicular, psi	17.3	20.8
Perpendicular, kPa	119.3	143.4
Parallel, psi	18.6	24.5
Parallel, kPa	128.2	168.9

[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

CONCLUSION

With the Montreal and Kyoto protocols in effect, the phaseout of 141b has accelerated in developing countries while the potential future phaseout of HFCs is imminent in developed countries. Polyurethane foam manufacturers are searching for a blowing agent that will allow them to meet current and anticipated regulations. Honeywell's HBA-2 liquid blowing agent will play an important role in this transition due to its low global warming potential (LGWP) and non-flammability. Polyurethane foams with HBA-2 offer comparable physical properties and better thermal insulation value when compared to foam with 245fa. Furthermore, HBA-2 demonstrates similar polyol miscibility as 245fa.

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BIOGRAPHY

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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 sector leader in the blowing agent technical service and development group with primary responsibility for panel and integral skin foam applications of fluorocarbon products.

David J. Williams
Dave holds a B.S. degree in Chemistry from the University of New Haven, New Haven, CT, USA. From 1975 to 1994, he worked as a Research and Development Chemist and a

Technical Service Representative for the Upjohn Company and later The Dow Chemical Company in a wide variety of rigid polyurethane and polystyrene foam application areas. Dave joined AlliedSignal (now Honeywell) in 1994 and is currently the senior manager of the Blowing Agent Technical Service and Development Group. In this capacity, he is responsible for technical service and product development of Honeywell's line of CFC, HCFC and HFC foam blowing agents. Dave is a member of the UNEP Flexible and Rigid Foam Technical Options Committee.