Honeywell

HBA-1 Blowing Agent Commercialization Status

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ABSTRACT

Honeywell International has developed and is commercializing a new, fourth generation polyurethane foam blowing agent (HBA-1) with attributes of very low global warming potential (GWP = 6) in conformance with the EU F-Gas Regulation. This blowing agent has evidenced efficacy in polyurethane foam applications, particularly one-component polyurethane foams. Further adoption is anticipated for the EU industry's applications requiring a high performance gaseous blowing agent and facing environmental restrictions. Application development of this blowing agent – including chemical and physical properties; performance and value; and health, safety and environmental considerations will be presented. Commercialization status update will be outlined.

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INTRODUCTION

The polyurethane foam insulation industry has utilized fluorocarbon blowing agents over the years due to a variety of desirable properties that these blowing agents impart to the foam and the application. In many applications, blowing agents that are gases at room temperature and pressure are preferred. Dichlorodifluoromethane (CFC-12) was the gaseous fluorocarbon blowing agent of choice until the phase out of this material due to its ozone depletion potential (ODP). Chlorodifluoromethane (HCFC-22) became the replacement for CFC-12 as it had similar desirable properties as a blowing agent and much lower ODP. In some applications, 1-chloro-1,1-difluoroethane (HCFC-142b) was utilized as a co-blowing agent, which while flammable, mitigated the high vapor pressure of HCFC-22. The industry was cognizant that HCFC's lifetime as a transition fluorocarbon blowing agents was limited due their ODP. HFC's were developed and commercialized as HCFC alternatives to meet requirements of zero ODP. For a portion of the one component foam industry in the EU that require a non-flammable, gaseous blowing agent, this molecule is 1,2,2,2-tetrafluoroethane (HFC-134a). Other HFC gases are commercially available which, while meeting the application requirements, exhibit undesirable properties of very high vapor pressure, flammability, or high GWP.

Honeywell conducted a research program to identify a fourth generation gaseous fluorocarbon blowing agent that would incorporate the desired environmental properties of zero ozone depletion potential (ODP) and low global warming potential (GWP), while maintaining desirable properties for polyurethane foams. To meet the requirements of the F-gas regulation, the one component foams industry required the attributes of a zero-ODP/low GWP blowing agent with properties that closely paralleled the chemical and physical properties of HFC-134a, namely non-flammability, moderate vapor pressure and reasonable solubility in polyols and prepolymer formulations used in the application. The molecule, designated as HBA-1, has been chosen for commercialization. HBA-1 possesses these

properties, along with favorable toxicity considerations, and the ability to commercially manufacture this molecule in a time frame that met the phase out of HFC-134a in EU one component foams industry in July 2008.

As of June 2008, HBA-1 has been commercialized in the EU. Manufacturing capacity has been completed, commercial operations have commenced, and EU inventory and supply chain logistics have been established. While the initial market to commence adoption of HBA-1 is the EU one component foam industry, broader acceptance of this molecule is being embraced in two component polyurethane foams and in the aerosol industry as an alternative to HFC-134a under EU regulatory pressures of global warming potential. Further, HBA-1 chemical and physical properties have been shown desirable in the extruded thermoplastic foam industry as a potential alternative to HFC-134a. In effect, HBA-1 is developing broad stature as the low global warming potential, non-flammable, environmentally desirable solution in foamed insulation products demanding a high performance blowing agent.

EU F-GAS REGULATION SYNOPSIS

The European Parliament and the Council of the European Union have committed the Community and its Member States to 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 (baseline) 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: certain HFC's (hydrofluorocarbons), PFC's (perfluorocarbons), and SF_6 (sulfur hexafluoride) as listed in Annex I (EC 842/2006) in one component foams "except when required to meet national safety standards". The exceptions to this list are "preparations" in which the weighted GWP is less than 150. This provision in regulations for EU one component foams became effective July 4, 2008 (Annex II to the Regulation).

Further to the preparation language, the intent of the Regulation is that "preparation" shall mean for the purposes of the obligations in this Regulation, excluding destruction, a mixture composed of two or more substances at least one of which is a fluorinated greenhouse gas, except where the total global warming potential of the preparation is less than 150. The total global warming potential of the preparation shall be determined in accordance with Part 2 of Annex I (an example is presented in the Annex of the published Regulation). In further unpublished as of yet clarification by DG Environment, "preparation" only includes the blowing agent and/or propellant components, and does not include components such as prepolymer in one component foams.

HBA-1 is in full compliance with the EU F-Gas regulation, in particular with respect to two matters: (1) it is not listed in Annex I as a fluorinated greenhouse gas, and therefore not covered by the provisions of the F-Gas regulation; and (2) the GWP of HBA-1 is 6, more than an order of magnitude less than 150.

Since the purpose and intent of the EU F-Gas Regulation is to control emissions of high GWP materials. HBA-1, with a GWP of 6, is in the same GWP range as many other materials that are considered as acceptable in inherently emissive applications, such as hydrocarbons. Therefore, HBA-1 is a solution to global warming potential issues facing the industry.

EU CHEMICAL SAFETY ASSESSMENT SYNOPSIS

EU New Chemicals Notification Requirements – 92/32/EEC (7th Amendment to Directive 67/548/EEC [OJEC L 154 of 05.06.1992]) outlines i.a. toxicity assessment requirement of new chemicals to the levels (quantity) of manufacture in the EU, import into the EU, and use in the EU. HBA-1 as of the writing of this paper has been notified at the Annex VIII – Level 1, which allows for supply into EU of 1000 tonnes/year or a cumulative of 5000 tonnes, before reaching the next notification level, i.e. Level 2. This quantity of HBA-1 is adequate to support the EU one component foam industry commencing July 2008. With respect to full commercialization of HBA-1 into EU one component foam industry, EU notification at the Annex VIII-Level 2, which allows for supply of HBA-1 quantities greater than 1000 tonnes/year or a cumulative of 5000 tonnes has been pre-empted and replaced by the REACH regulation.

REACH regulation [Registration, Evaluation, Authorisation and Restriction of Chemicals, (EC) 1907/2006] has, effective June 1, 2008, replaced the notification provisions of directive 67/548/EEC. Under REACH each manufacturer or importer of a substance over 10 metric tonnes per year is obliged to submit a registration file, including a chemical safety assessment. For volumes over 100 and 1000 metric tonnes, 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. HBA-1 has been notified for use in insulation foam and as an aerosol propellant.

The main effect of REACH is that legacy substances (which are on the EINECS, European Inventory of Existing commercial Chemical Substances) that were exempted from the notification obligations under Directive 67/548/EEC will have to be registered. For these phase-in substances, a transition period is applicable depending on the volume band and their classification.

Substances on the ELINCS, including HBA-1, are considered as registered under REACH (article 24) for the volume band for which they have been notified. In the case of HBA-1, this means that Honeywell can place up to 1000 metric tonnes on the European market without any further obligation under REACH.

Prior to exceeding the tonnage band, each registrant must submit an update to the registration file. Honeywell intends to submit an update for the 1000+ metric tonnes status early in 2009. Within three weeks of receipt, the European Chemicals Agency (ECHA, based in Helsinki, Finland) must conduct a completeness check of the registration (update). This is a formal check if the registrant has fulfilled all the formalities under REACH, it is not an evaluation of the data provided. If the registration is considered as complete, the registrant may produce or import the substance in the quantities for which it has submitted the registration (update).

The evaluation of the registration file will be dependent on the characteristics of the substance and the intended uses. Toxic chemicals, or substances intended for emissive use by the general public will be giver greater priorities than substances that are notified for non-emissive, or professional/industrial use. Such an evaluation may lead to possible restrictions on use, labeling requirements or other measures intended to prevent undesirable exposure of humans and the environment.

CHEMICAL AND PHYSICAL PROPERTIES OF HBA-1

HBA-1 is a blowing agent/propellant material exhibiting zero ozone depletion, very low global warming potential, and non-flammability. HBA-1 is a moderate pressure gas at standard temperature and pressure. The properties of this material are provided in Table 1 For comparative purposes Table 1 illustrates the properties of HBA-1 in perspective with other commonly used one component foam blowing agent / propellants. Figure 1 illustrates the vapor pressure of HBA-1 in relation with other currently utilized blowing agents / propellants in this application.

Table 1. *Blowing Agent / Propellant Comparative Properties*

Property	HBA-1	HFC-134a	HFC-152a	DME	iso-butane
Molecular Weight	<125	102	66	46	58
Boiling Point (°C/°F)	<-15 / < 0	-26/-15	-25/-13	-23/-13	-12 / 11
Flash Point (°C/°F)	None (at room temperature)	None	<-50 /<-58	-41/-42	-83/-117
LEL/UEL (Vol% in air)	None	None	3.9/16.9	3.4/18.0	1.8/8.4
	(measured at room temperature ~ 21°C)				
ODP	0	0	0	0	0
GWP (100 yr horizon)	< 15	1300	140	<15	<15

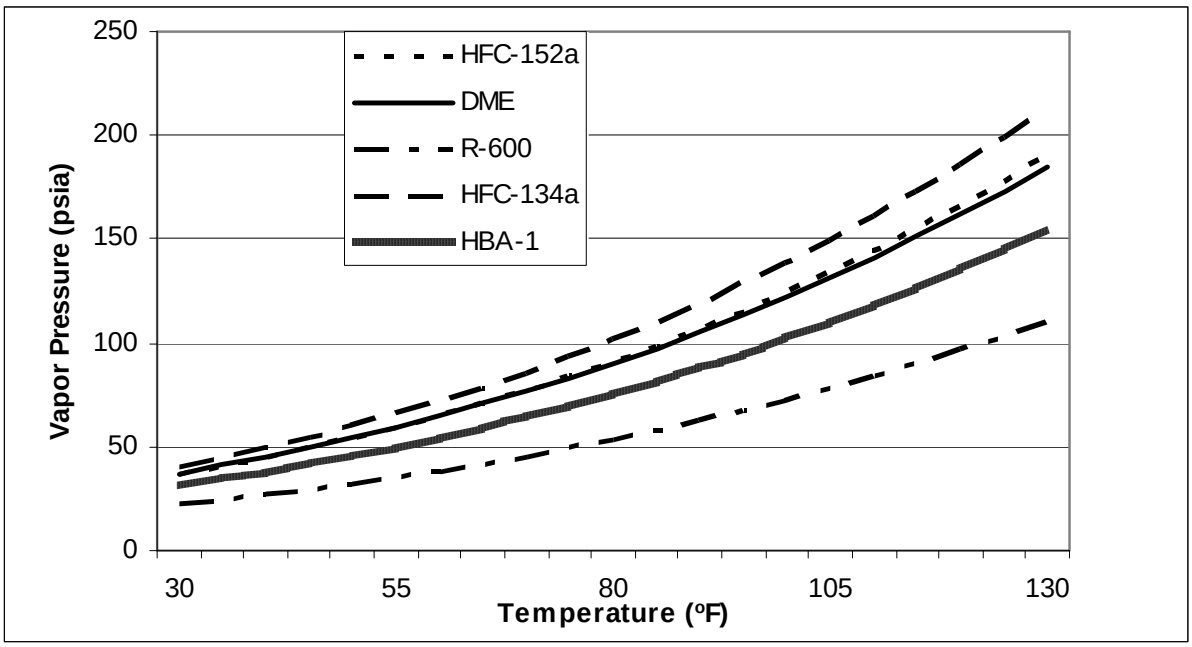

Figure 1. *HBA-1 Vapor Pressure*

TOXICITY ASSESSMENT

HBA-1, at the writing of this paper, is significantly down the path of risk assessment for use and commercialization as might be anticipated by the EU notification level discussed earlier. Table 2 illustrates the encouraging results suggesting a low order of toxicity for HBA-1.

Table 2. **HBA-1** ***Toxicology Assessment***

Test	Results
Cardiac Sensitization	No Effect to 120,000 ppm
Genetic Testing	
Mouse micronucleus	Not active at 100,000 ppm
Ames assay	Not active at 50,000 ppm
Acute Inhalation	
4 hour: mice	100,000 ppm; No Lethality
4 hour: rat	400,000 ppm; No Lethality
Chromosome aberration test:	Not Active
Inhalation: 2 week	Test Complete
Inhalation: 4 week	Test Complete
Unscheduled DNA Synthesis	
4 week @ 15,000 (rat)	Not Active
Bone Marrow Micronucleus Formation	
4 week @ 15,000 (rat)	Not Active
Cancer Screen	Test Complete
Metabolism Study	Underway
Inhalation: 13 week	Test Complete
Teratology Study	Test Complete

FLAMMABILITY DISCUSSION

HBA-1 is a non-flammable gas by test methods ASTM E-681, and by EU Test method A-11. Flammability characterization of HBA-1 was performed by Chilworth Technologies Ltd – UK, with the finding "It has been concluded beyond reasonable doubt that the material (HBA-1) will not possess oxidizing or explosive properties".

It should be noted that flammability characterization and flammability regulations for gaseous materials are evaluated at room temperature ~ 21°C. It should also be recognized that non-flammable materials such as HFC-134a and HCFC-22 at elevated temperature or pressure exhibit flame limits. This phenomenon is exhibited by HBA-1 at elevated temperatures. Above 28°C flame limits, while relatively narrow, become apparent. At 30°C, HBA-1 exhibits flame limits LEL/UEL at 7.0/9.5 volume percent in air.

COMPATIBILITY OF MATERIALS

HBA-1 is non-reactive and non-corrosive toward all commonly used metals in polyurethane processing and one component foams package filling equipment. This includes carbon steel, stainless steel, copper and brass. This assessment was performed by immersing metal coupons in neat HBA-1 in a sealed tube, and held at elevated temperatures (400°F [200°C] and 600°F [315°C]) for two weeks.

HBA-1 is comparable to HFC-134a with respect to compatibility with commonly used plastics and elastomers. Honeywell investigated compatibility of plastics and elastomers by immersing test coupons in neat HBA-1 in a sealed tube at room temperature for a period of two weeks. The sealed tubes, under pressure, exposed the substrate to the liquid and gas phases of HBA-1. It should be noted, however, that other components such as polyurethane pre-polymer were not evaluated, as formulations vary by manufacturer. The results of this compatibility study are summarized in Table 3.

Table 3 Materials Compatibility with HBA-1

Substrate	Average Percentage Change		
	Hardness	Weight	Volume
Plastics			
HDPE		+0.82	-3.74
Polypropylene		+0.83	0.0
PVC – Type 1		+0.01	-0.44
PET		-0.01	0.0
Polyetherimide		-0.04	0.0
Nylon 6,6		-0.26	0.0
PVDF		+0.21	0.0
PTFE		+2.03	+2.43
Elastomers			
Fluoroelastomer	-11.29	+4.43	+5.71
Nitrile Rubber	+8.91	-4.95	-7.18
EPDM	-1.50	-2.00	-2.49
Butyl Rubber	-1.13	+1.27	+0.88
Neoprene	+7.32	-7.70	-11.47

Notes: Fluoroelastomer = Viton B: Trademark of DuPont Dow Elastomers
PVDF = Kynar: Trademark of Atofina Company
PTFE = Teflon: Trademark of E.I DuPont Company
Polyetherimide = Ultem: Trademark of General Electric Company

ONE COMPONENT FOAM APPLICATIONS

The EU one component foam industry currently utilizes a variety of blowing agents/propellants, with the specific choice driven by performance. In this industry, performance is generally defined in terms of non-flammability of blowing agent/propellant; quality of foam, most importantly an even/fine cell structure, dimensional stability, and ability to apply in severe temperature conditions (e.g. winter conditions). Specific applications requirements define the value proposition for HFC-134a and HBA-1 as a replacement for HFC-134a.

HBA-1 has been assessed by multiple EU one component foam manufacturers. While formulations vary, and in some cases significantly, in general HBA-1 has been found to be an efficacious replacement for HFC-134a. Figure 2 illustrates the comparison of HBA-1 to HFC-134a in one component foam.

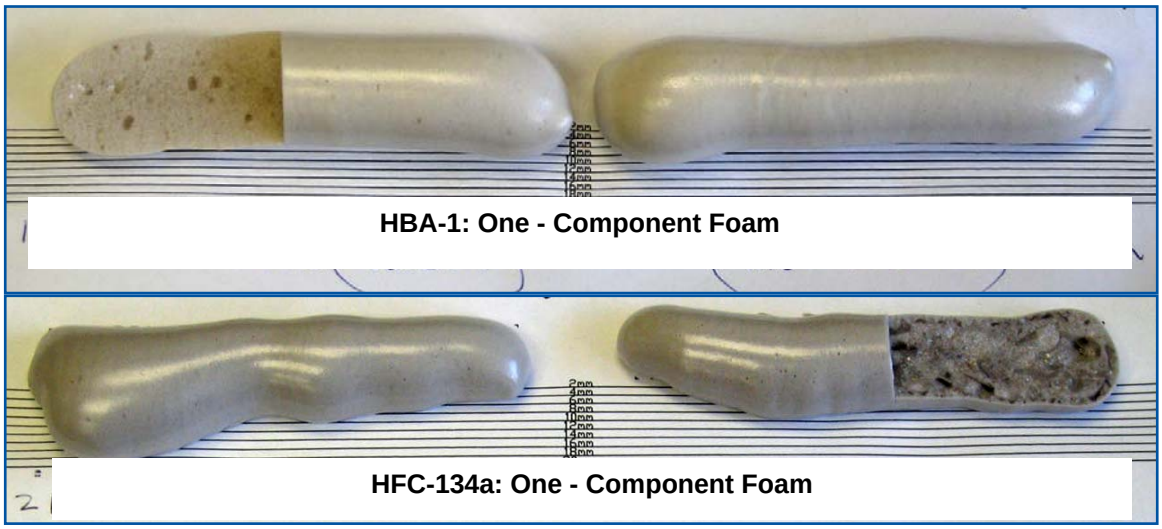

Figure 2. *One Component Foam Comparison*

Note the difference in cell uniformity and structure between the two foams. HBA-1 clearly adds quality / performance to this application.

TWO COMPONENT POLYURETHANE FOAMS

HBA-1 exhibits good performance as a blowing agent in conventional two component polyurethane foams, with foam thermal performance similar to HFC-134a in various formulations. Solubility of HBA-1, across a spectrum of polyols, generally suggests improved characteristics over HFC-134a. Those familiar with foamed polyurethane processes will observe that gaseous blowing agents are more easily incorporated utilizing third stream blowing agent addition prior to, or directly at the foam head. HBA-1 will find direct application in polyurethane applications wherein HFC-134a is dosed into the polyol stream, as a co-blowing agent, to enhance frothing characteristics and performance.

HBA-1 COMMERCIALIZATION STATUS

At the writing of this paper, Honeywell has successfully commercialized HBA-1 in the EU coinciding with the implementation of the EU F-Gas Regulation constraints on the use of high GWP materials in one component foams industry. The manufacturing site is located at Buffalo, NY, USA, with inventory and terminal in both NA (for export) and the EU. Commercialization in other regions of the world is dependent upon completion of notification and registration requirements for the respective regions.

As environmental regulations restrict or limit the use of high GWP materials, HBA-1 has applications in adjacent industry segments requiring the chemical and physical attributes of HBA-1. For example, the EU F-Gas Regulation will impact the EU novelty aerosol industry in July 2009, for which HBA-1 will offer a non-flammable, gaseous solution.

With respect to U.S. commercialization, HBA-1 SNAP (Significant New Alternatives Policy) application has been submitted to the U.S. EPA for approval, in compliance with Section 612 of the Clean Air Act. HBA-1 PMN (Pre Manufacturing Notice) has been submitted. SNAP and PMN approvals are required for commercialization in the U.S.

CONCLUSIONS

With the EU F-Gas Regulation constraints on use of high GWP materials, such as HFC-134a having commenced July 4, 2008, many European one component polyurethane manufacturers are finding commercial utility in the use of HBA-1 to achieve performance objectives. Honeywell has provided data relative to physical and chemical properties of HBA-1, along with materials compatibility data, and a walk through commercialization timeframe.

Honeywell's intent is continued commercialization of HBA-1 prior to restrictions on the use of HFC-134a in the various polyurethane segments and adjacent industries.

BIOGRAPHIES

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Jim holds a B.S. degree in Chemical Engineering from Iowa State University, Ames, IA, a M.Eng. degree from McNeese State University, Lake Charles, LA, a MBA from Northern Illinois University, DeKalb, IL, and is a registered professional engineer in the State of Louisiana. Jim joined Allied Corporation (AlliedSignal, now Honeywell) in 1984 and has worked in sales, marketing, commercial development, and technical service capacities. He is currently a senior principal engineer in Honeywell's Blowing Agent Technical Service and Development Group with primary responsibility for appliance industry applications of fluorocarbon products.

D. 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 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 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.