Low Climate Change Impact Solution: Household Refrigerators / Freezers

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ABSTRACT

Honeywell has developed a preliminary construct for a highly energy efficient refrigerator utilizing ultra low global warming potential (GWP less than 15) materials, in the manner of blowing agent for the polyurethane foam insulation and refrigerant working fluid inclusive.

On a global basis, the industry, individual government regulators, and NGOs are continually striving for a low environmental impact energy solution across all energy consuming applications, including household refrigerators. This preliminary solution outlines the climate change impact imparted from not only indirect contribution (energy consumption), and includes, additionally, the direct contribution to climate change from the associated raw materials utilized in manufacture of household refrigerators. The solution description will characterize the energy consumption performance, the manufacturing considerations in a modern refrigerator factory, and the risks associated with flammability perspective in manufacturing and consumer use.

INTRODUCTION

Amongst the numerous raw materials utilized in the manufacture of household refrigerator, refrigerator/freezer, and freezer industry, included are: 1) refrigerant gas, as the working fluid in the refrigerant circuit; and 2) blowing agent, as the insulation gas in the polyurethane foam insulation. The phase out of ozone depleting substances (ODS) in this industry has lead to the use of two categories of materials – hydrofluorocarbons (HFC) and hydrocarbons (HC). The use of certain HFC materials in this industry is particularly attractive due to a variety of desirable properties exhibited or imparted by HFC materials. R-134a (1,1,1.2-tetrafluoroethane) refrigerant gas has been widely favored due to the high flammability characteristics of the alternative gas R-600a (isobutane). HFC-245fa (1,1,1,3,3-pentafluoropropane) blowing agent has gained wide acceptance due to the excellent thermal performance imparted to the polyurethane foam insulation, and the flammability characteristics of the alternative blowing agents (hydrocarbons). One of the major detriments to the heretofore iterated HFC materials is the concern of the global warming potential (GWP).

The household refrigerator industry has a hierarchy of attributes for refrigerants and blowing agents:

- good environmental properties and low global warming potential (GWP)
- low order of toxicity
- high performance, specifically with respect to efficiency and capacity for refrigerant gases, and thermal performance for blowing agents
- non-flammable, or low flammability risk characteristics
- commercial availability on a global basis

All other attributes equal, the refrigerator OEM would generally choose the highest performance material, for a variety of reasons, however most importantly higher performance material use allows more freedom for an individual refrigerator energy platform design.

Honeywell embarked upon a research program to identify fourth generation halocarbon chemistry that would incorporate the desired environmental properties, that is, low global warming potential (GWP) with respect to climate change, while maintaining desirable properties and high performance characteristics. The EU F-Gas Regulation (for those applications specifically listed / regulated) may require a GWP less than 150. Further, with respect to blowing agents in the context of end of lifetime management, embedded in the Waste Electronic and Electrical Equipment

(WEEE) directive (2002/96/EC) is the concept of a GWP less than 15. These new high performance materials, while containing fluorine, are also by their chemical structure classified as olefins, or, more specifically halo-alkenes. These new materials are a separate and distinct class of materials from the heretofore known HFC materials, primarily due to the olefin nature of the molecule and the relatively short lifetime in the atmosphere. More specifically, in IUPAC nomenclature: 1234ze(E) is [trans-1,3,3,3-tetrafluoropropene], 1234yf is [2,3,3,3-tetrafluoropropene], and HBA-2 is [a proprietary developmental liquid material].

LOW GWP MATERIALS PHYSICAL PROPERTY COMPARISON

As discussed earlier, in the manufacture of household refrigerators/freezers in North America, HFCs; 245fa blowing agent and 134a refrigerant gas have been favored due to the high performance attributes of these materials for this application. Illustrated in Table 1, Honeywell HBA-2 blowing agent exhibits physical properties similar to 245fa, and 1234yf refrigerant gas exhibits very similar properties to 134a refrigerant. It would be noted that the global warming potential (GWP) of both HBA-2 and 1234yf is more than two orders of magnitude lower than that of currently utilized HFCs, both are more than one order of magnitude lower than the present limitations in the EU F-Gas Regulation, and within the rationale of the EU WEEE Directive pertaining to household refrigerator/freezers, with a GWP less than 15.

Table 1. Low GWP materials Comparative Physical Properties

	PUR Blowing Agents		**Refrigerant Gases**	
Property	**HBA-2**	245fa	1234yf	134a
Molecular Weight	**< 134**	134	**114**	102
Boiling Point (°C)	**15 <T_{BP}< 30**	15.3	**–30**	–26
LFL / UFL (vol%-air)	**None**	None	**6.2 – 12.3**	None
GWP (100 yr)	**7**	1030*	**4**	1430*

*2007 Technical Summary. Climate Change 2007: The Physical Science Basis. Contribution of Working Group 1 to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change.

LOW CLIMATE CHANGE IMPACT HOUSEHOLD REFRIGERATOR / FREEZER

Honeywell has reported in various proceedings on the commercial development of LGWP blowing agents in the various polyurethane (PUR) applications, including appliance foams. PUR foam properties of lambda (k-factor), compressive strength, and dimensional stability derived from characterization of hand mix foams or foam panels prepared by means of a high pressure foam machine have evidenced efficacy in comparison to 245fa foams. This type of development effort to develop baseline data is necessary to conjecture the performance in the commercial manufacture of refrigerators, refrigerator/freezers, and freezers. However, until commercial refrigerator product has been manufactured under industrial conditions, and assessed for energy performance and ancillary performance in other aspects, for example, liner compatibility, adhesion to liner and metal cabinet and doors, freeze stability, and other quality aspects, an OEM cannot make a prudent decision that a commercially viable, 'real world' solution is available.

To that end, a scale trial, utilizing Honeywell HBA-2 blowing agent, in a commercially available polyurethane system, in a commercially available 710 liter (25 ft^3) household refrigerator freezer was undertaken. These thirty two refrigerator cabinets, with associated door sets, were foamed to investigate:

- Lambda (k-factor) performance in various locations of the refrigerator
- Liner compatibility: High Impact Polystyrene (HIPS)
- Dimensional stability
- Freeze stability at target density
- Compressive strength
- Adhesion: plastic liner material and metal case
- Foam closed cell content

- DOE (Department of Energy) Energy Performance
    - Energy consumption with 134a refrigerant working fluid
    - Energy consumption with 1234yf refrigerant working fluid

The baseline comparison for these low climate change impact refrigerators is the same commercial household refrigerator/freezer product utilizing 245fa blowing agent and 134a refrigerant. It should be noted that:

- Polyurethane formulation: HBA-2 was equal molar substituted for 245fa. No other modifications were made to the PUR system
- R-134a sealed side loop: No modifications were made
- R-1234yf sealed loop: minor modifications were made to the capillary tube diameter and length

Polyurethane Foam Formulation

As discussed prior, the polyurethane formulation was a commercially available, and currently utilized, 245fa appliance formulation, supplied by a major PUR systems house, with HBA-2 equal molar substituted for 245fa. The foaming process conditions, including machine temperatures and pressure were identical to the conditions for the 245fa baseline cabinets and doors. The polyurethane formulation and process parameters are illustrated in Table 2. Those familiar with refrigerator factories and scale will observe the scale of foam through put is consistent to scale found in North American world-scale factories, and is consistent with the size refrigerators manufactured in this trial.

HBA-2 processed very similarly to 245fa, and no modifications were made to the PUR foaming equipment or process, effectively, conventional existing PUR equipment, existing in the factory, accommodated HBA-2.

Additionally, characterization of the HBA-2 versus 245fa foamed cabinets and doors suggest no differences:

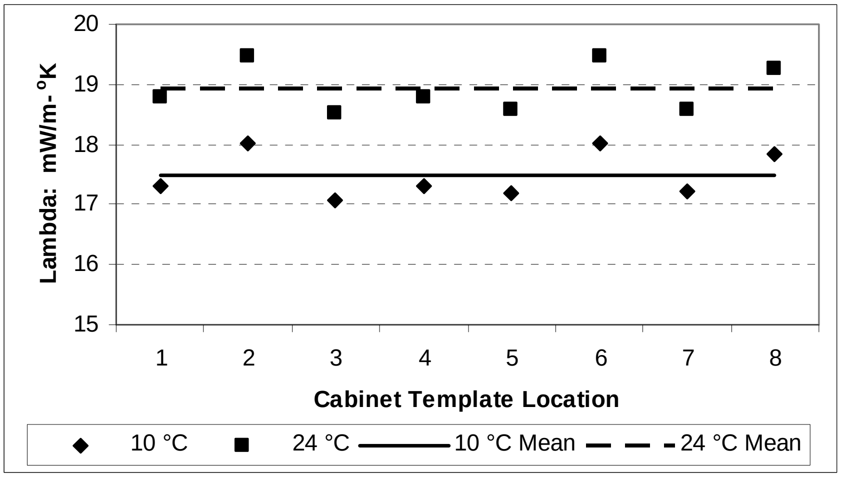
- Minimum fill weights were nearly identical – within one quarter of one percent (0.25%)
- Over pack conditions (lambda / k-factor assessment) were identical at 10%
- Density (10% over pack) Cabinets: 34.9 kg/m³ (2.18 lbs/ft³) Doors: 34.1 kg/m³ (2.13 lbs/ft³)

Table 2. Appliance PUR Formulation and Process Parameters

Component	245fa (% wt)	HBA-2 (% wt.)
Polyol Blend	71.3	→
Additives	4.3	→
Water	1.0	→
Blowing Agent	23.4	Equal Molar
Isocyanate	100	→
Door Foam Rate: kg/min (lbs/min)	40.8 (90)	40.8 (90)
Cabinet Foam Rate: kg/min (lbs/min)	90.7 (200)	90.7 (200)
B-Side Temperature °C (°F)	18.3 (65)	18.3 (65)
A-Side Temperature °C (°F)	23.9 (75)	23.9 (75)
Gel Time (sec)	25.0	24.0
Tack Free (sec)	33.0	31.0
Injection Pressure MPa (psi)	10.4 (1500)	10.4 (1500)

Lambda (k-factor) Performance

Foam samples from various locations in the fresh food compartment and freezer compartment were assessed for lambda (k-factor) performance. PUR foam thermal conductivity can, and will vary throughout the refrigerator/freezer due to foam flow characteristics and associated density variation. Graph 1 illustrates the lambda (k-factor) performance in eight different locations of the refrigerator/freezer. It would be noted that the variation is not significant, and that the mean (average) lambda (k-factor) is: 17.5 mW/m-°K at 10 °C [0.121 BTU-in/ft²-°F (50 °F)] and 18,9 mW/m-°K) at 24 °C [0.131 BTU-in/ft²-°F (75 °F)]. In conjunction with PUR thermal conductivity performance, consideration of the closed cell content of foams is useful in understanding thermal conductivity variation, and that open cell content is not sufficient to cause compressive strength or dimensional stability issues in the longer term. The closed cell content analysis is shown in Table 3, and is in excess of 90% closed cells.



Graph 1. Refrigerator/Freezer lambda in various locations

Table 3. Refrigerator PUR Foam Open Cell / Closed Cell Content ***ASTM D-6226***

Cabinet Location	% Open Cell	% Closed Cell
Top	5.9	91.7
Fresh Food # 1	5.6	92.0
Fresh Food # 2	6.5	91.1
Fresh Food # 3	6.2	91.2
Fresh Food # 4	6.4	91.1
Fresh Food # 5	6.8	90.7
Freezer # 1	5.3	92.3
Freezer # 2	9.9	87.8
Freezer # 3	9.6	88.1
Freezer # 4	10.9	86.8
Mullion	4.8	92.6
Mean	7.1	90.5

1) PUR Foam Density: 34.9 kg / m^3 (10% over pack)
2) Typical Acceptable Open Cell Content: 10%
3) Polymer % content is the remainder to 100% (Polymer Mean % Content = 2.4%)

Compressive Strength Performance

Polyurethane foam in refrigerator freezers provides, firstly insulation performance, however, also provide structural strength for the appliance. Appliance PUR foams typically exhibit compressive strength greater than 100 kPa (15 psi) at 10% deflection. Samples were taken from varying locations in the fresh food and freezer compartments to assess compressive strength, and are shown in Table 4.

Table 4. Refrigerator PUR Foam Compressive Strength		*ASTM D-1621*
Cabinet Location	**Parallel (kPa / *psi*)**	**Perpendicular (kPa / *psi*)**
Fresh Food #1	118.3 / *17.15*	113.5 / *16.45*
Fresh Food #2	124.5 / *18.05*	123.2 / *17.85*
Freezer #1	138.7 / *20.10*	117.6 / *17.05*
Freezer #2	180.4 / *26.15*	161.5 / *23.40*
Mean	140.5 / *20.36*	129.0 / *18.69*

1) Compressive strength: @ 10% deflection
2) PUR Foam Density: 34.9 kg/m³ / *2.18 lbs/ft³* (10% over pack)
3) Typical acceptable value: > 103.5 kPa / *15 psi*

Dimensional Stability Performance

Continuing the logic of mechanical properties of refrigerator/freezers, dimensional stability of the PUR foam is important as a quality measure. Changes in foam dimensions (volume) when subjected to temperature variation impacts the external metal case, the internal liner, and should the volume change due to temperature difference be extreme, impacts the adhesion characteristics to the metal case and liner. Refrigerator/freezer appliances, particularly in the freezer section, are subjected to wide temperature difference between the compartment interior and ambient room temperature in the home. PUR foam samples from various locations in the fresh food and freezer compartments were assessed for volume change at temperature extremes over 1 day and 7 day interval, and exhibited less than 1% average volume change, and the results are shown in Table 5.

Table 5. Cabinet PUR Foam Dimensional Stability			*ASTM D-2126*	
Cabinet Location	**Dimensional Stability (% Volume Change)**			
	1 day (-30 °C)	1 day (70 °C)	7 day (-30 °C)	7 day (70 °C)
Fresh Food #1	+0.70	–0.55	+0.25	–0.35
Fresh Food #2	+0.10	–0.30	–0.55	–0.60
Freezer #1	+0.05	–0.90	–0.55	+0.05
Freezer #2	–2.40	–0.75	–1.40	+0.00
Mean	–0.39	–0.63	–0.56	–0.23

1) PUR Foam Density: 34.9 kg/m³ (10% over pack)
2) Typical Allowable Foam Volume Change: 3.0 %

Plastic Liner (HIPS) Compatibility

Plastic liners, either high impact polystyrene (HIPS) or acrylonitrile butadiene styrene (ABS) are currently utilized in household refrigerators/freezers, though, steel liners are used in some specific refrigerator designs and freezers. Differing liner materials (excepting steel) exhibit varying compatibility to PUR foams. Liner compatibility is dependent upon a wide variety of variables: plastic thickness, extrusion of the plastic sheet conditions, thermoforming or vacuum forming conditions, amongst others, and not the least, the blowing agent. Chlorofluorocarbons (11), hydrochlorofluorocarbons (141b, 142b, and 22), and hydrofluorocarbons (245fa and 134a), as well as hydrocarbon blowing agents all exhibited quite varying compatibility with either HIPS or ABS liner material. Liner compatibility to PUR foams containing new blowing agents is a significant concern, as correcting liner compatibility, while not an insurmountable problem, can result in added cost to the OEM.

Unfortunately, there is no confident method of a priori assessing refrigerator liner materials without building a refrigerator, subjecting the refrigerator to thermal cycling, and subsequently assessing the liner for blistering and cracking. High impact polystyrene (HIPS) liner material was utilized in this refrigerator trial.

- Four refrigerator/freezers with doors were thermal cycled in a cold room chamber
- Hot cycle: 54 °C (130 °F) for 10 hours
- Cold cycle: -34 °C (-30 °F) for 10 hours
- Five consecutive days

Upon completion of the five days thermal cycling protocol, the HIPS liners did not exhibit, and were free of, blisters, cracks, or any visual degradation.

DOE Energy Assessment

The U.S. Department of Energy (DOE) established, in July 2001, a standard (DOE Standard) for the maximum energy consumption of household refrigerators. In simplified terms (reader is referred to Federal Register 10CFR 430 for more detail) the standard allows a maximum energy usage by refrigerator internal volume, adjusted for various accessories, such as though the door water and ice dispensers. In addition, the DOE provides for the Energy Star label for refrigerators, refrigerator/freezers, and freezers, which, as of March 2008 is DOE Standard minus 20% energy consumption. Further, presently the DOE is in the process of establishing, for promulgation in 2014, a revised and presumably more stringent energy standard for household refrigerators, refrigerator/freezers, and freezers.

All the lambda (k-factor) assessments aside, meeting the DOE Energy Standard determines whether a refrigerator meets the energy requirements to be sold in the U.S. The refrigerator/freezers manufactured in this trial not only met the DOE Standard, not only met the DOE Energy Star label, but exceeded the Energy Star label requirements by an average of 7.6%, effectively DOE Standard minus 27.6%. Five refrigerator/freezers utilizing HBA-2 blowing agent / 134a refrigerant were assessed by the DOE Energy Star test method. Five refrigerators/freezers utilizing 245fa blowing agent / 134a refrigerant was the baseline comparison, that on average, exceeded DOE Energy Star label by 6.0%. Effectively, the HBA-2 refrigerator/freezers showed an energy reduction of 1.6% from the baseline, with the results (normalized) illustrated in Chart 1.

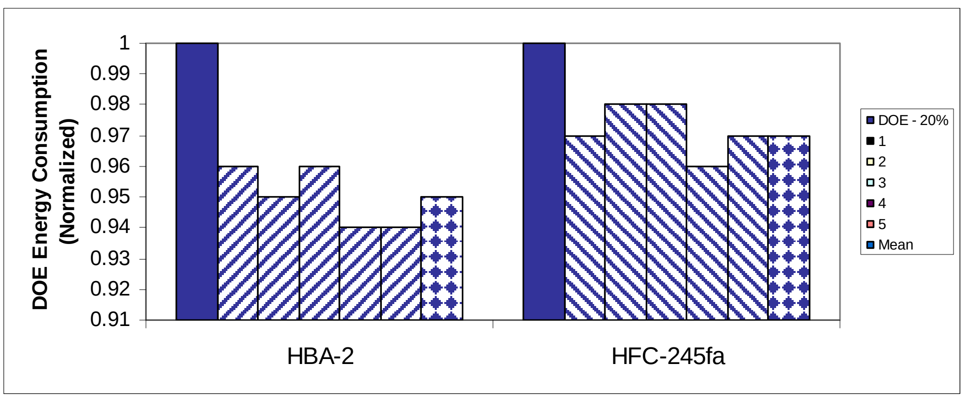


Chart 1. DOE Energy Efficiency Performance

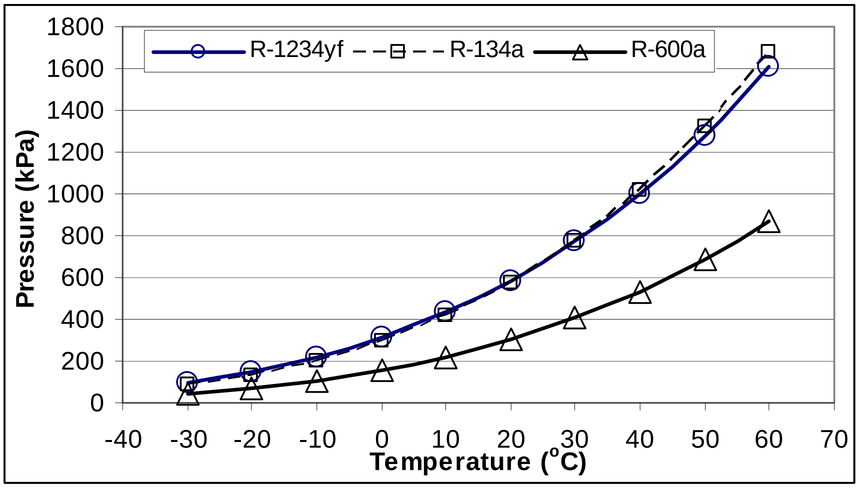
Sub-Summary: Household Refrigerator Energy Performance utilizing HBA-2 Blowing Agent

Commercially manufactured 710 liter (25 ft^3) household refrigerator/freezers with HBA-2, equal molar substituted for 245fa, in a commercially available 245fa appliance PUR formulation, exceeded the DOE Energy Star performance criteria, and, exceeded the 245fa baseline performance.

HBA-2, in all ancillary assessment related to a household refrigerator/freezer, met or exceeded all requirements, that is liner compatibility, compressive strength, dimensional stability, and freeze stability.

LOW GWP REFRIGERANT ASSESSMENT: R-1234yf

After significant evaluation and testing, Honeywell identified R-1234yf as the low GWP refrigerant gas of choice for this work due overall ability of the molecule to compare favorably in performance and other relevant characteristics to R-134a. For example, Graph 2 shows a good pressure-temperature curve match for R-1234yf and R-134a refrigerants, whereas R-600a is a much lower pressure refrigerant gas. It should be noted, however, that refrigerant boiling point and corresponding pressure-temperature curves are only one of the overall mosaic of chemical properties and performance attributes that ultimately define the efficacy, and overall suitability for use, of a refrigeration working fluid. Additionally, mechanical design characteristics of the compressor, heat exchangers (condenser and evaporator), and expansion devices significantly impact the energy efficiency performance in a household refrigerator application.



Graph 2. Refrigerant Pressure – Temperature Relationship

Further to characterization of refrigerant working fluids suitability is thermal stability with compressor lubricants under extreme conditions of temperature and moisture (water) contamination. R-1234yf and a typical appliance compressor oil – ISO 10 (Proeco 10S) were evaluated utilizing ASHRAE Standard 97 test method. Under extreme conditions of high moisture (1000 ppm); high temperatures (200°C); and two week duration, visual examination of the sealed tubes (containing R-1234yf / lubricant) exhibited no change in the appearance. Analysis of the oil yielded very low acidity values (TAN values ranging from 0.07 to 0.44); and, GC analysis and molecular weight analysis of the refrigerants indicated no change in the purity. Thus concluding that R-1234yf is stable, used in conjunction with typical lubricants for these applications.

Simulations utilizing a semi-theoretical model: Cycle-11 UA (Domanski and McLinden 1992) confirmed R-1234yf as a near drop-in replacement to R-134a in this refrigerator/freezer application. Table 6 illustrates the simulation comparison of R-1234yf to R-134a.

Table 6. Refrigerant Assessment in Household Refrigerators

Refrigerant	Displ.	Capacity	Eff.	$Flow_{Mass}$	P_d/P_d	UA, ev.	UA, cd	ΔP_{Evap}	ΔP_{Cond}	T_{Evap}	T_{Cond}
134a	100	100	100	100	100	100	100	100	100	100	100
1234yf	100	107	102	130	87	104	119	119	136	100	99

1) R-1234yf 'drop-in' example
2) R-134a baseline = 100%

Expansion Devices

Mass flow differences shown in Table 6, suggest modifications in capillary tubes. An analysis of capillary tubes was performed utilizing ASHRAE RP 948 model, which is based on Buckingham Pi dimensionless number. This model accounts for both thermodynamic and transport properties of the refrigerant.

Simulations were performed for typical design conditions of –23°C evaporation temperature, 0°C superheat at the evaporator outlet, and 32.2°C compressor inlet temperature. The condensing temperature was 55°C with 5°C sub-cooling at the condenser outlet. Previous system simulations determined the 'target' mass flow, allowing R-1234yf to equal R-134a capacity. Table 7 illustrates simulations for the drop-in assessment, and for modified capillary tube diameter assessment, while maintaining the same characteristic overall length. The R-134a baseline calculations are a capillary tube: 0.66 mm diameter; 2.7 m length; of which 1.622 m is in contact with the suction line.

Five refrigerator/freezers (710 liter / 25 ft³), PUR foamed with HBA-2, were built up for energy performance utilizing R-1234yf replacement for R-134a. Minor modifications to the capillary tube diameter and length were made prior to foaming the refrigerator/freezer with HBA-2 PUR foam. These low GWP refrigerators are in assessment at this writing.

Table 7. Capillary tube / Suction Line Heat Exchanger

Refrigerant	From Evap. (m)	Heat Exch (m)	To Comp (m)	Diameter (mm)	Mass Flow (kg/hr)	Mass Flow (%)	Target (%)
R-134a	0.898	1.622	0.180	0.66	4.335	100.0	
1234yf drop-in	0.898	1.622	0.180	0.66	4.116	94.9	
1234yf modified	0.898	1.622	0.180	0.71	4.978	114.8	130.0

1) General guidelines: charge optimization will allow equilibrium balance of capillary tube & refrigerant flow.

Sub-Summary: Household Refrigerator Energy Performance utilizing R-1234yf

R-1234yf, as a potential R-134a replacement, is attractive for numerous reasons, including its ability to equal or exceed R-134a in energy efficiency performance, as well as being a low GWP refrigerant fluid, with minor (sic low manufacturing cost) modifications in a NA style household refrigerator/freezer. Further, R-1234yf utilization significantly mitigates the risk associated with utilization of highly flammable hydrocarbon refrigerants, such as R-600a.

ENVIRONMENTAL and REGULATORY SYNOPSIS

The United States Congress has commenced developing climate change bills which, while still too early to predict the final structure and language, will in all probably impact high global warming potential materials in some fashion. To varying degrees, industry is preparing solution scenarios to meet current and future 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 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 or greater which include certain HFC's (hydrofluorocarbons), PFC's (perfluorocarbons), and SF_6 (sulfur hexafluoride) as listed in Annex I (EC 842/2006). The EU F-Gas Regulation will be reviewed in 2011, which may results in additional use restrictions for high GWP fluids (Article 10, F-Gas Regulation).

These materials; 1234yf, 1234ze(E), and HBA-2 are in full compliance with the EU F-Gas regulation, in particular with respect to two matters: (1) they are 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 these materials is 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. 1234ze(E), with a GWP of 6; 1234yf, with a GWP of 4; and HBA-2, with a GWP of 7 are in the same GWP range as many other materials that are considered as acceptable in inherently emissive applications, such as hydrocarbons. Therefore, these materials are a solution to global warming potential issues facing the industry. Furthermore, electrical appliances are subject to the EU Ecodesign framework directive (2009/125/EC, a recast of the original EuP Directive, 2005/32/EC). Under this framework directive specific rules (implementing measures) may be adopted for a certain category of energy using products, such as domestic refrigerators with a view to achieve a low life-cycle impact on the environment. In this context, the availability of low GWP fluids can be expected to taken into consideration

Japan has made Kyoto Protocol commitments to reduce, or limit emissions of greenhouse gases, though has not formally promulgated domestic regulations to enforce these commitments.

Low GWP materials, in the context of atmospheric lifetime, often prove to be volatile organic compounds (VOC), 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 is that of ethane. The MIR of these materials has been measured at less than the value for ethane, hence are expected to be classified as non-VOC in the US (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 POCP = 12.3, (Nielsen, University of Copenhagen) as 1234yf: POCP = 7.0 and 1234ze(E): POCP = 6.4, with HBA-2 estimated to be in this range.

CHEMICAL SAFETY ASSESSMENT (REGISTRATIONS for USE) SYNOPSIS

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 application for Pre Manufacturing Notification (PMN). Approval of the PMN, then includes the material's listing on the Toxic Substances Control Act (TSCA) inventory. Further, materials to be used in the various 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 a chlorofluorocarbon (CFC) prior applications legacy. 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) status contained in CAA, flammability codes, and other requirements. R-1234yf applications for both PMN approval and SNAP listing have been made to the EPA, and at this writing, 1234ze(E) has been SNAP listed in various applications. At this writing, HBA-2 filing for SNAP and PMN is anticipated in 2010 year.

In the European Union, 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 1 metric tonne per year is obliged to submit a registration file, including a chemical safety assessment for volumes greater than 10 tonnes. 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. R-1234yf has been notified for use as a refrigerant gas, and 1234ze(E) has been notified for use in one component foam, insulation foam, as an aerosol propellant, and as a refrigerant gas, and the REACH inquiry for HBA-2 has been filed.

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 1234yf and 1234ze(E), are considered as registered under REACH (article 24) for the volume band for which they have been notified. For both 1234yf and 1234ze(E) updates have been submitted under REACH, permitting unlimited quantities to be placed on the European market..

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. These requirements have been fulfilled, such that Honeywell can import 1234ze(E), and 1234yf into Japan without volume or use restrictions, and no special controls or monitoring are required. HBA-2 documentation has been filed in Japan at this writing.

Other regions of the world, individually, have requirements for toxicology assessment and environmental impact assessment prior to commercialization of new materials.

TOXICITY ASSESSMENT

At the writing of this paper, 1234yf is significantly down the path of risk assessment for use and commercialization as might be anticipated by the U.S EPA SNAP and PMN submissions, as well as the EU notification level discussed earlier. R-1234yf has a low order of toxicity, and is classified as 'A' [low toxicity] by ASHRAE.

HBA-2 is early in the process of toxicological assessment protocols, in a similar fashion to 1234yf and 1234ze(E). While this assessment is in the early stages, preliminary toxicity assessment data is promising for this molecule. The status of the toxicity evaluation to date is shown in Table 8.

Table 8. HBA-2 Toxicology Assessment	
Test	Results
Cardiac Sensitization	Test Complete
Genetic testing:	
Ames Assay	Test Complete
Mouse Micronucleus	Test Complete
Acute Inhalation (Rat, 4 hour)	Test Complete
Inhalation: 2 week	Test Complete
Inhalation: 4 week	Test Complete
Unscheduled DNA synthesis	Test Complete

FLAMMABILITY DISCUSSION

HBA-2 is a non-flammable liquid by ASTM E-681 test methods, and exhibits no flashpoint or vapor flame limits. In transportation, storage, and in factory use as a blowing agent, HBA-2 has no limitations on hazards classification.

R-1234yf is a flammable gas. However, the flammability characterization, and associated risk in use, of R-1234yf is significantly different from highly flammable hydrocarbon refrigerants, for example R-600a (isobutane). The significance centers in: the minimum ignition energy (very high for R-1234yf / very low for R-600a); the heat of combustion (low for R-1234yf / high for R-600a); and burning velocity, or flame speed (very slow for R-1234yf / very high for R-600a). ASHRAE characterization of flammability: R-134a = A1; R-600a = A3; while R-1234yf = A2L (A2 category of flammability, however, very low in that category). The significant differences in flammability measures between R-1234yf and R-600a are shown in Table 9.

Table 9. Flammability Characterization: R-1234yf v. R-600a (isobutane)

	LFL (vol %-air) (at 23°C)	UFL (vol%-air) (at 23°C)	Minimum Ignition Energy (mJoules)	Heat of Combustion (kJ/kg)	Burning Velocity (cm/sec)
R-1234yf	6.2	12.3	>5000/<10000	10,730	1.5
R-600a	1.8	8.4	0.52	45,680	40.0

LOW GWP COMMERCIALIZATION STATUS

At the writing of this paper, Honeywell has successfully commercialized 1234ze(E) in the EU coinciding with the implementation of the EU F-Gas Regulation constraints on the use of high GWP materials, and 1234ze(E) commercialization in Japan is underway.

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 submitted. SNAP and PMN approvals are required for commercialization in the U.S.

R-1234yf is registered in the EU under REACH to greater than 1000 tonnes level, and is in the commercialization process. With respect to U.S. commercialization of 1234yf, the SNAP and PMN applications have been submitted to the U.S. EPA.

HBA-2 is in the EU REACH inquiry stage, has been filed for compliance with Japan Chemical Substances Control Law, and at this writing, Honeywell anticipates SNAP and PMN filing with the U.S. EPA by year end of 2010.

CONCLUSIONS

With the global attention to climate change, and potential restrictions on the use of high GWP blowing agents and refrigerant gases in the various regions of the world, Honeywell has demonstrated a preliminary construct, in the context of a North American design platform [710 liter (25 ft^3)], for a highly energy efficient household refrigerator/freezer utilizing ultra low global warming potential (GWP less than 15) materials, in the manner of blowing agent for the polyurethane foam insulation and refrigerant working fluid inclusive. Unlike hydrocarbon blowing agent and refrigerant gases, HBA-2 and R-1234yf achieve comparable energy performance to existing HFC materials without significant design or hardware modifications.

Honeywell's intent is continued commercialization of low environmental impact solutions for the appliance industry, as well as other industries requiring high performance halochemical solutions.

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 and safety measures are indicated herein or that other measures may not be required.

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BIOGRAPHIES

J. M. Bowman, P.E.

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.

S. F. Yana Motta

Samuel holds a B.Sc degree ini mechanical engineering from National Engineering University of Peru , with PhD degree obtained from Catholic University – Rio de Janeiro, Brazil. Professional experience includes 6 years as a project engineer in Lima Peru, a 1.5 year period as a visiting scientist at the National Institute of Standards and Technology (Thermal Machinery Group). Samuel joined Honeywell in 2000, and is a senior principal engineer with current responsibilities for management of the refrigerant applications laboratory located in Buffalo, NY.