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HFO-1234yf Low GWP Refrigerant Update Honeywell / DuPont Joint Collaboration

Mark Spatz

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International Refrigeration and Air Conditioning Conference at Purdue July 14-17, 2008



- DuPont And Honeywell Have Identified HFO-1234yf (CF₃CF=CH₂) As The Preferred Low GWP Refrigerant Which Offers The Best Balance Of Properties And Performance
- Other Auto Industry Options Have Certain Limitations
 - CO₂: complexity, energy efficiency and requires mitigation
 - 152a / secondary loop: performance, size and weight



Excellent environmental properties

- Very low GWP of 4, Zero ODP, Favorable LCCP
- Atmospheric chemistry determined and published

Low toxicity, similar to R-134a

- Low acute and chronic toxicity
- Significant testing completed

System performance very similar to R-134a

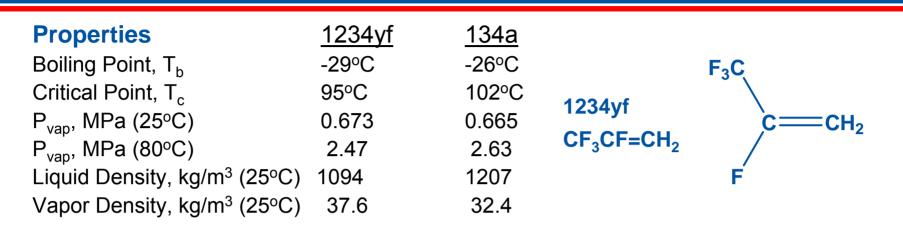
- Excellent COP and Capacity, no glide
 - From both internal tests and OEM tests
- Thermally stable and compatible with R-134a components
- Potential for direct substitution of R-134a

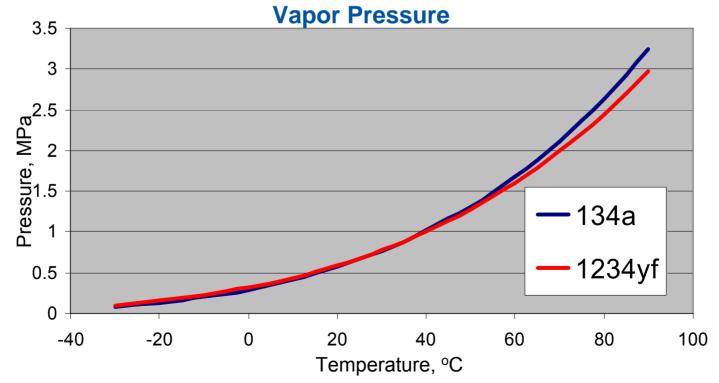
Mild flammability (manageable)

- Flammability properties significantly better than 152a; (MIE, burning velocity, etc)
- Potential for "A2L" ISO 817 classification versus "A2" for 152a based on AIST data
- Potential to use in a direct expansion A/C system better performance, lower weight, smaller size than a secondary loop system

HFO-1234yf Properties

Honeywell



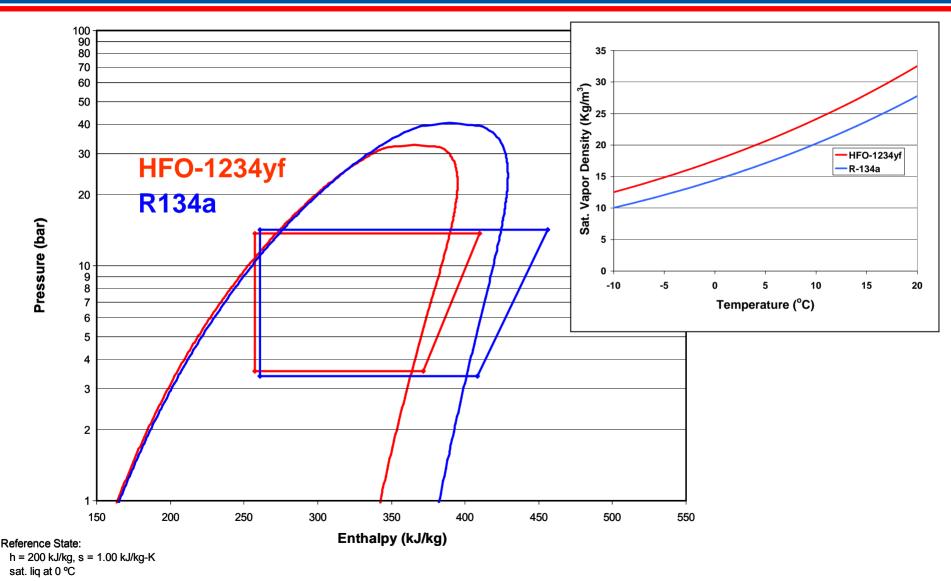


The miracles of science"



Thermodynamic Analysis Typical MAC Condition

Honeywell



Similar Capacity – Lower H_{fg} but Higher Vapor Density



Excellent Environmental Properties

- ODP = 0
- **100 Year GWP = 4** (GWP_{134a} = 1300)
 - Measurements completed & published:
 "Atmospheric Chemistry of CF₃CF=CH₂"
 Chemical Physics Letters <u>439</u> (2007) pp 18-22
- Atmospheric lifetime = 11 days

Atmospheric chemistry measured

- Atmospheric breakdown products are the same as for 134a
- No high GWP breakdown products (e.g. NO HFC-23 breakdown product)
- Results published in 2008
- Good LCCP

Available online at www Scien USPUER Chemical Physics Lette	ceDirect	CHEMICAL PHYSICS LETTERS
		www.elsevier.com/locate/cple
Atmospheric chemistry of CF ₃ C	F=CH ₂ : Kinetics and	mechanisms
of gas-phase reactions with	그는 말에서 가지 🖷 이번 것을 많은 것이 집에서 가지 않는 것을 하는 것이다.	
O.J. Nielsen ^{a,*} , M.S. Javadi ^a , M.P T.J. Wallingto	. Sulbaek Andersen ^a , M.D. on ^{b,*} , R. Singh ^c	Hurley ^b ,
* Department of Chemistry, University of Copenhage ^b Physical and Environmental Sciences Department, Ford M ^c Honeywell International Inc., 101 Co		
Received 31 January 200	7; in final form 6 March 2007 ine 21 March 2007	
Abstract Long path length FTIR-smog chamber techniques were $k(OH + CF_{C}F=CH_{2}) = (1.05 \pm 0.17) \times 10^{-12}$, and $k(O_{3} + CF_{2}$ N ₂ , N ₂ /O ₂ , or air diluent at 296 K. CF ₂ CF=CH ₂ has an atmosph (100 yr time horizon) of four. CF ₂ CF=CH ₂ has a negligible globs radiative forcing of climate change. © 2007 Elsevier B.V. All rights reserved.	$CF=CH_2$ = (2.77 ± 0.21)×10 ⁻²¹ cm ³ mo eric lifetime of approximately 11 days and	decule ⁻¹ s ⁻¹ in 700 Torr o I a global warming potentia
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Long path length FTIR-enong chamber techniques were $k(0H - CF_{C}CE=CH) = (1.05 \pm 0.17) \cdot 10^{-1}$, and $k(0) + CF_{F}$ N_{2} , N_{2} , N_{2} or $i a ti diment a 126 K. CF_{C}C=CH_{2}$ has a nategoight (10) yr time horizon) of four. CF_{C}C=CH_{2} has a negligible globe radiative forcing of climate change. 2007 Elsevier B.V. All rights reserved. 1. Introduction Recognition of the adverse environmental impact of chlorofluorocarbon (CFC) release into the atmosphere	CP=CH ₂] = (2.77 ± 0.21)×10 ⁻²¹ cm ³ m re: Efetime of approximately 11 days and d warming potential and will not make an tion with ozone and (iv) atmosph are reported herein. 2. Experimental	lecule ⁻¹ s ⁻¹ in 700 Torr o a global warming potentia y significant contribution to
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Significant Toxicity Information Available

Test	HFO-1234yf	134a	
 Acute Lethality 	No deaths 400,000 ppm	No deaths 359,700 ppm	\checkmark
 Cardiac sensitization 	NOEL > 120,000 ppm	NOEL 50,000 ppm LOEL 75,000 ppm	\checkmark
 13 week inhalation 	NOEL 50,000 ppm	NOEL 50,000 ppm	\checkmark
Developmental (Rat)	NOAEL 50,000 ppm	NOAEL 50,000 ppm	\checkmark
Genetic Toxicity	Not Mutagenic	Not Mutagenic	\checkmark
 13 week genomic (carcinogenicity) 	Not active (50,000 ppm)	Baseline (50,000 ppm)	\checkmark
 Environmental Tox 	NOEL > 100 mg/L (Pass)	NOEL > 100 mg/L (Pass)	\checkmark

HFO-1234yf Has Low Toxicity



ATEL Calculation

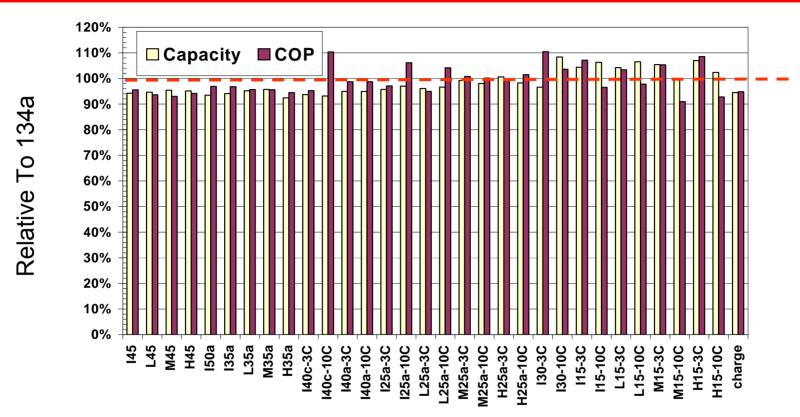
- ATEL (Acute Toxicity Exposure Limit) is a value used by standards organizations (e.g. ASHRAE 34) to reduce the risks of acute toxicity hazards in normally occupied spaces.
- It is calculated from the acute toxicity data for a given refrigerant and provides an estimate of the maximum exposure limit for a short time period (e.g. 30 minutes)

Refrigerant	ATEL (ppm)		
R-12	18,000		
R-134a	50,000		
R-152a	50,000		
CO ₂	40,000		
HFO-1234yf	101,000		

HFO-1234yf Has a Favorable ATEL Value



System Bench Test Results Honeywell



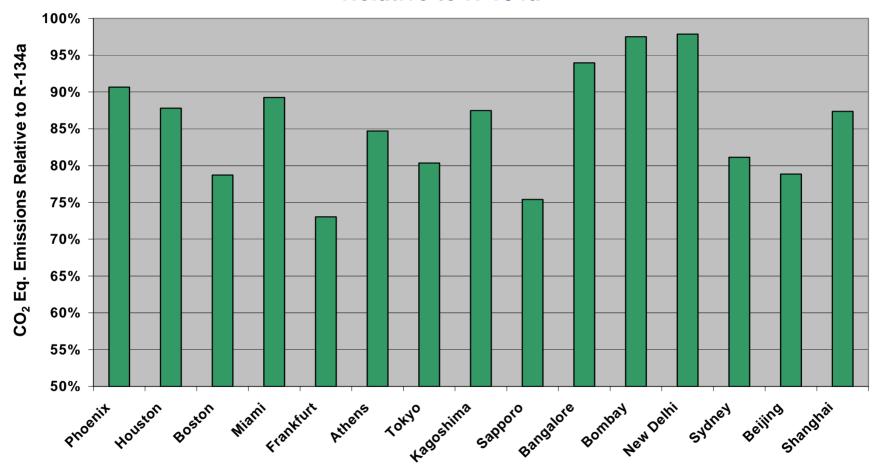
- · No changes were made to system including TXV; Industry standard test conditions
- Both Capacity and COP are generally within 5% of 134a performance.
 - This was recently confirmed at two outside labs.
- Lower compression ratio, low discharge temperature (12°C lower at peak conditions)
- Further improvements likely with minor system optimization, for example:
 - Lower ΔP suction line and / or TXV optimization to maintain a more optimum superheat.

HFO-1234yf performance is comparable to 134a; further improvement possible with minor optimization

HW/DuPont Data



Relative to R-134a



Average 15% Better LCCP Values; Up to 27% in Europe JAMA and FIAT Obtained Similar Results





1234yf: Excellent Plastics Compatibility ND8 PAG at 100°C for two weeks

Refrigerant	Plastics	Rating	24 h Post Weight Chg. %	Physical Change
1234yf	Polyester	1	4.4	0
"	Nylon	1	-1.5	1
"	Ероху	1	0.3	1
"	Polyethylene Terephthalate	1	2.0	0
"	Polyimide	0	0.2	0

Refrigerant	Plastics	Rating	24 h Post Weight Chg. %	Physical Change
R134a	Polyester	1	5.6	0
"	Nylon	1	-1.4	1
п	Ероху	1	0.3	1
"	Polyethylene Terephthalate	1	2.8	0
"	Polyimide	0	0.7	0

Rating 0 = best when weight gain < 1 and physical change = 0

1 = borderline when weight gain > 1 and < 10 and/or physical change upto 2

2 = incompatible when weight gain > 10 and/or physical change = 2





1234yf: Excellent Elastomers Compatibility

ND8 PAG at 100°C for two weeks

Refrigerant	Elastomers	Rating	24 h Post Linear Swell %	24 h Post Weight Gain %	24 h Post Delta Hardness
1234yf	Neoprene WRT	0	0.0	-0.3	1.0
"	HNBR	0	1.6	5.5	-7.0
"	NBR	0	-1.2	-0.7	4.0
"	EPDM	0	-0.5	-0.6	4.0
"	Silicone	1	-0.5	2.5	-14.5
"	Butyl rubber	0	-1.6	-1.9	0.5
Refrigerant	Elastomers	Rating	24 h Post Linear Swell %	24 h Post Weight Gain %	24 h Post Delta Hardness
R134a	Neoprene WRT	0	-0.6	-1.3	2
"	HNBR	0	2.1	8.6	-5.5
"	NBR	0	0.0	3.0	-3.5
"	EPDM	0	-1.1	-0.4	-2
"	Silicone	0	-1.4	1.4	-2.5
II	Butyl rubber	0	-1.1	-1.6	-3.5

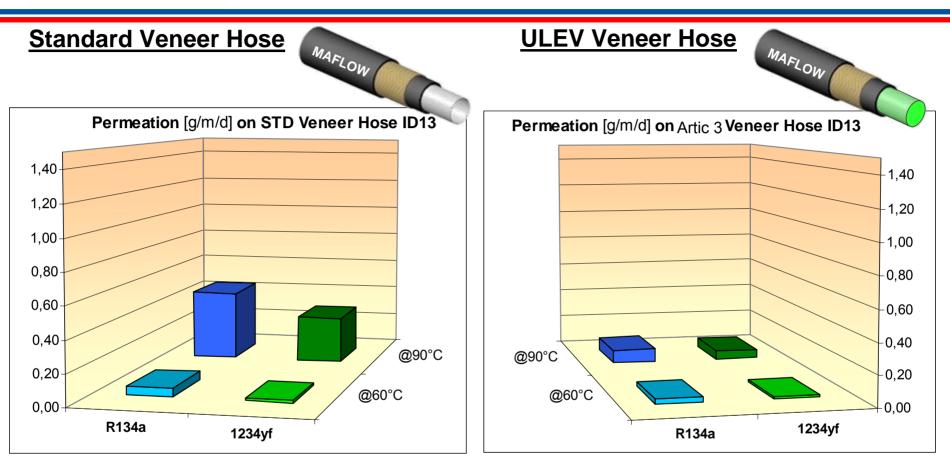
Rating

0 = best when weight gain < 1 and physical change = 0

1 = borderline when weight gain > 1 and < 10 and/or physical change upto 2

2 = incompatible when weight gain > 10 and/or physical change = 2

The miracles of science^T Permeation HFO-1234yf vs R-134a Honeywell



<u>Results</u>

HFO-1234yf shows lower permeability values toward Veneer hoses compared to R134a.

<u>Remarks</u>

With the same gas concentration (0.6g/cm³) the inner pressure with HFO-1234yf is lower (e.g: at 90°C was -20%)

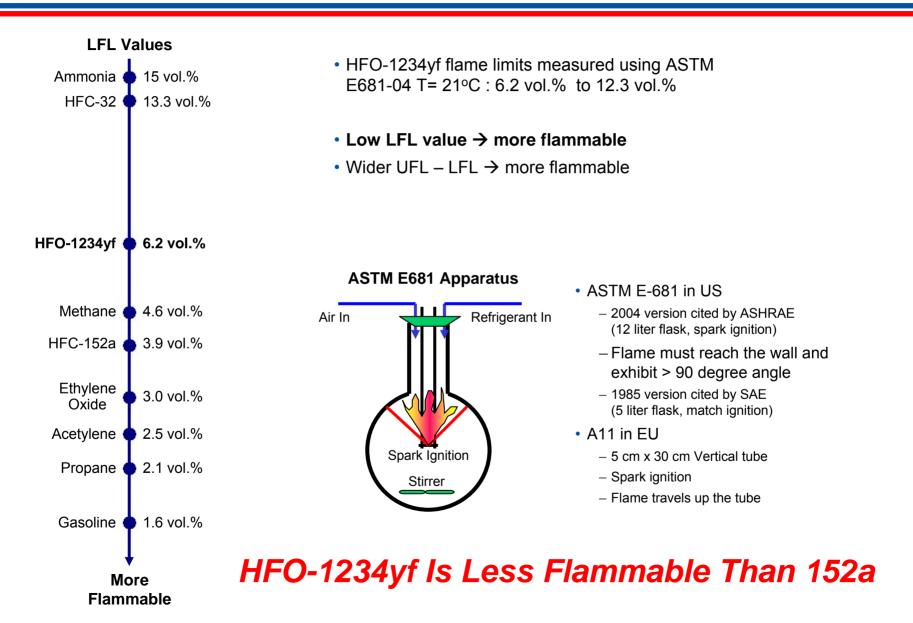




Refrigerant Flammability Tests

- Is it flammable? If yes, Flame Limits will exist.
 - LFL lower flammability limit
 - UFL upper flammability limit
- What is the probability of an ignition source being present of sufficient energy to cause an ignition?
 - Autoignition temperature
 - Minimum ignition energy (MIE)
- What is the impact (damage potential) if an ignition occurs?
 - Heat of combustion
 - Burning velocity

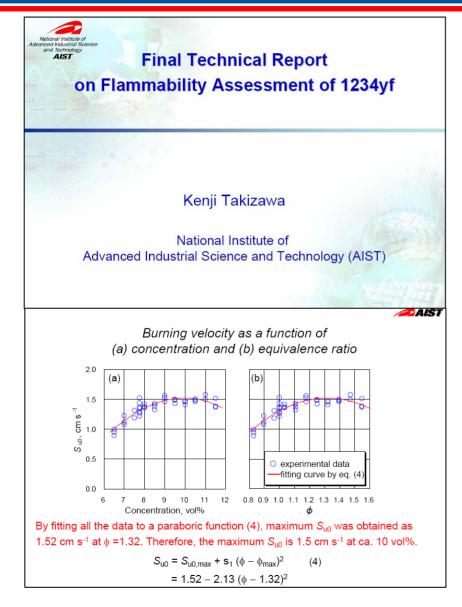


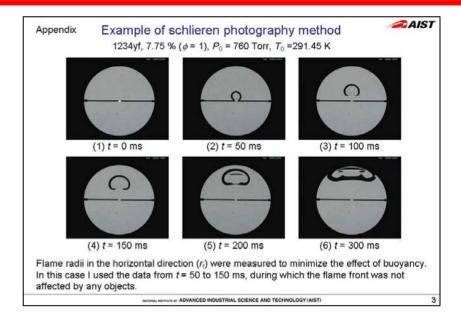




Burning Velocity

Honeywell





Burning Velocity Measurements

- · Measurements performed in 3 liter spherical apparatus
- Experimental result for HFO-1234yf: 1.5 cm s⁻¹
- ISO 817 Flammability Classification is 2L (lowest flammable class classification)

	Propane	152a	$\rm NH_3$	32	1234yf
BV, cm s ⁻¹	46	23	7.2	6.7	1.5*



Minimum Ignition Energy

- 12-liter glass sphere used in ASTM E681 flammability limit tests was modified for MIE testing in order to eliminate potential wall quenching effects seen in standard 1 liter vessel
- Materials Tested:
 - HFC-32 from 16-22% (v/v) in 1% increments at 30 and 100 mJ nominal
 - HFO-1234yf from 7.5-11% (v/v) in 0.5% increments up to 1000 mJ nominal
 - Ammonia at 22% (v/v) at 100 and 300 mJ nominal

<u>Refrigerant</u>	No Ignition Occurred	Ignition Occurred
HFC-32	<mark>30</mark> +/- 12 mJ	<mark>100</mark> +/- 30 mJ
Ammonia	<mark>100</mark> +/- 30 mJ	<mark>300</mark> +/- 100 mJ
HFO-1234yf	<mark>5,000</mark> +/- 350 mJ	10,000 +/- 350 mJ

HFO-1234yf Is Very Difficult To Ignite With Electrical Spark



HFO-1234yf Mild Flammability Properties

	LFL ^a (vol%)	UFL ^a (vol%)	Δ (vol%)	MIE) (mJ)	BV ^c (cm/s)
Propane	2.2	10.0	7.8	0.25	46
R152a	3.9	16.9	13.0	0.38	23
R32	14.4	29.3	14.9	30-100 ^b	6.7
Ammonia	15	28	13	100-300 ^b	7.2
HFO-1234yf	6.2	12.3	5.8	5,000-10,000 ^b	1.5

Flammability Properties

^aFlame limits measured at 21 C, ASTM 681-01

^bTests conducted in 12 litre flask to minimize wall quenching effects ^cBurning Velocity ISO 817 (HFO-1234yf BV measured by AIST, Japan)

Flammability Index

	R	F	RF	RF2
HFO-1234yf	0.97	0.27	3.6	0.6
32	1.31	0.33	4.6	2.3
152a	1.78	0.5	16.6	17.9
Propane	1.99	0.55	56.7	37.2

$$R = \frac{Cst}{LFL}$$

$$F = 1 - \sqrt{\left(\frac{LFL}{UFL}\right)}$$

$$RF = \left[\sqrt{\left(\frac{UFL}{LFL}\right)} - 1\right] \times \frac{Q}{M}$$

$$RF2 = \left\{\left(\sqrt{(UFL \times LFL)} - LFL\right) / LFL\right\} \times Qst \times Su$$

Cst = Stoichiometric composition in air, vol.%

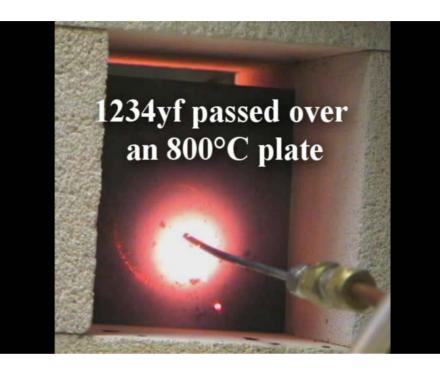
- Q = Heat of Combustion per one mole
- Qst = Heat of Combustion per one mole of the Stoichiometric mixture, kJ/mol
- Su = Burning speed in Meters/Second
- M = Molecular weight



Autoignition Temperature & Hot Surface Ignition



- The autoignition temperature of HFO-1234yf was determined at Chilworth Technology in UK.
 - Uniformly heated 500 ml glass flask, observed in dark for 10 mins.
 - Autoignition temperature for HFO-1234yf determined to be 405°C.
- Note that the air refrigerant mixture must be at this temperature for ignition to occur.



- Experiments were conducted to evaluate the ignition potential of hot surfaces (up to 800°C) to cause ignition.
 - 6 mm steel plate heated from behind with propane-oxygen torch
 - No ignition seen

- HFO-1234yf vapor sprayed onto the plate
- Infrared Thermometer measured temperature.
- Three "dots" seen are to aim the thermometer • Occasional red circles are diffraction rings from the camera lens reflecting the red plate through the refractive index gradient (caused by hot air / cold refrigerant).





Summary of Hot Plate Tests

			Hot Manifold	
		550°C <mark>Faint Red</mark>	800°C Cherry Red	>900°C Orange
	Spray No oil	No ignition	No ignition	No ignition
HFO-1234yf	Premixed with air no oil	Not tested	No ignition	No ignition
	with PAG oil	No ignition	No ignition	Ignition
	Spray no oil	No ignition	No ignition	No ignition
R-134a	Premixed with air no oil	Not tested	No ignition	No ignition
	with PAG oil	No ignition	No ignition	Ignition

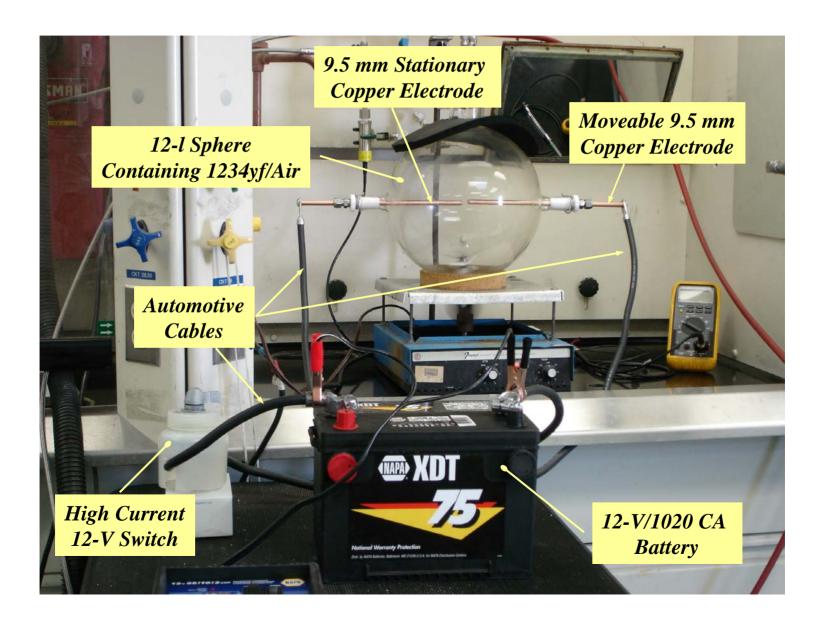
HFO-1234yf shows same flammability behavior as R-134a -Ignition due to presence of oil



HFO-1234yf Ignitability to Spark from 12-V Battery Short Circuit

- A potential ignition source for potentially flammable refrigerant/air leaks in passenger compartment of cars is a spark caused by a short circuit from a 12-V battery located under the seat
- The purpose of these tests is to determine whether such a spark is capable of igniting an 'optimum' concentration of HFO-234yf in air
- Follow procedures from ASTM E681 to prepare a well-blended refrigerant/air mixture of a known concentration in a sealed 12-I spherical flask; add moisture equivalent to 50% RH at 23° C
- Create a short-circuit in the mixture by discharging a high-capacity 12-V automotive battery (1020 cranking amps) across 9.5 mm diameter copper electrodes located in the sphere
- Perform tests for 8.13, 8.5, and 9.0% HFO-1234yf concentrations at 20°C, 60°C and 80°C; non-ignitions to be confirmed by nine (9) additional trials









Battery Ignition Results

- <u>No ignitions</u> observed at 8.13, 8.5, and 9.0% HFO-1234yf at either 20°, 60° or 80°C (10 trials per concentration)
- For comparison the ignitability of ammonia, a refrigerant of relatively low flammability, was tested at a 20% v/v concentration at 20°C and 60° C; positive test was obtained on the first trial

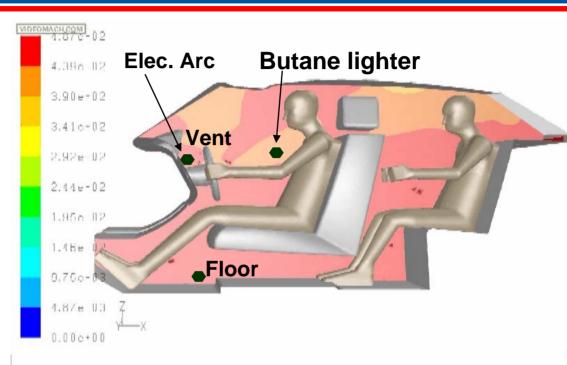


Passenger Compartment Evaluations

- As shown in the previous charts, the flammability parameters were conducted under very tightly controlled conditions.
 - Well mixed, uniform concentration of refrigerant and air.
 - Stagnant, not flowing environment.
 - Fixed conditions (e.g. temperature)
- In actual applications these conditions do not exist.
- Evaluations both experimental and with computer simulations were conducted to try to more closely approximate real world conditions.

The miracles of science^{*} CFD Modeling/Mockup Testing Honeywell

- Good agreement between prediction and measurements.
- No increase in flame length from butane lighter.
- No flame from Electrical Arc.



Contours of volume_fraction_ref (lime=6.0000c+02) Nov 26, 2007 FLUENT 6.3 (3d, dp, pbns, spc, rkc, unsteady)

	60 sec		360 sec		600 sec	
	CFD	Test	CFD	Test	CFD	Test
Vent	1.0	0.2	3.5	3.5	4.5	2.4
Floor	1.5	1.4	4.1	3.6	4.5	3.3
Butane Lighter	NO	NO	NO	NO	NO	NO
Elec. Arc	NO	NO	NO	NO	NO	NO



Extreme Leak Results: No Ignition with Arc Welder

- With simulated ruptured tube leak
 - No ignition with arc welder on floor (simulating battery ignition source)
 - No ignition with arc welder at vent outlet (simulating PTC heater ignition source)





Results of Mock-up Flammability Tests

Test No.	Test Description	Ignition Source	Time of Ignition	Result
	Large Corrosion Leak (0.5 mm	diameter)		
1	Cigarette lighting at breath level	Butane lighter	After leak starts	No Ignition - only flame color change noted
2	Pooling Test- no blower operation	Arc welder on floor	Four minutes after end of leak	No Ignition
3	Cigarette Lighting at Vent Outlet	Butane lighter	After leak starts	No Ignition - only flame color change noted
		diamotor)		
4	Ruptured Tube Leaks (6.4 mm Cigarette lighting at breath level	Butane lighter	After leak starts	Butane lighter failed to light.
4	· 、	<i>.</i>	After leak starts After leak starts	Butane lighter failed to light. No ignition
	Cigarette lighting at breath level	Butane lighter		
5	Cigarette lighting at breath level Simulation of battery short	Butane lighter Arc welder on floor	After leak starts	No ignition
5	Cigarette lighting at breath level Simulation of battery short Simulation of PTC heater short	Butane lighter Arc welder on floor Arc welder at vent outlet	After leak starts After leak starts	No ignition No ignition



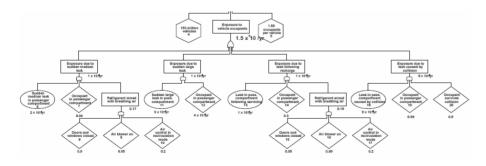
CFD Modeling & Flammability Testing Conclusions

- CFD Modeling
 - Good agreement for refrigerant concentration profiles between CFD and mock-up tests
- Mock-up test results
 - Ignition of HFO-1234yf did not occur, even with:
 - worst case leak representing evaporator rupture where LFL was exceeded
 - high energy ignition sources (butane lighter and arc welder)
- Results of hot surface tests at 800 C simulating engine compartment hot manifold showed no ignition.
 - Consistent with engine compartment test results from the CRP-1234 program
- No ignition occurred from 12V battery spark
- This is likely due to low burning velocity and high MIE of HFO-1234yf which makes it difficult to sustain and propagate a flame

HFO-1234yf Flammability Risk is Very Low



- For most fires to happen, fuel and air at the right <u>concentration</u>, and an ignition source, with a sufficient <u>energy level</u> must co-exist at the <u>same</u> <u>place</u> and in the <u>same time</u>.
- Several risk assessments have been completed or are in progress in US (SAE CRP-1234), Japan (JAMA) and Europe utilizing inputs of modeling and leak experiments
 - ✓ Release Experiments
 - Cabin and underhood
 - Normal operation and crash condition
 - Service (Professional and DIY)
 - CFD modeling to visualize concentration distribution for various scenarios.



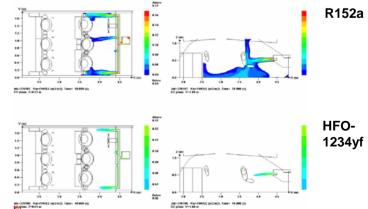




Table 26. Risks of Injury or Fatality from Various Events Compared to Risks Associated with Leaks of HFO-1234yf				
Risk	Risk per year	Citation		
Risk of stroke	2.7 x 10 ⁻³	Rhys Williams, 2001		
Fatal accident in the home	1.1x 10 ⁻⁴	Wilson and Crouch, 1987		
Fatal accident while climbing mountains (if mountaineer)	6 x 10 ⁻⁴	Wilson and Crouch, 1987		
Risk of being injured as a pedestrian	2.1 x 10 ⁻⁵	NSC, 2004		
Fatal injury at work (all occupations)	3.6 x 10⁻⁵	NSC, 2004		
Injury from lightning strike	1 x 10 ⁻⁶	NWS, undated**		
Risk of being fatally injured in an elevator ride	2x10 ⁻⁷	McCann and Zalesky, 2006		
Risk of exposure to HFO-1234yf above health based limits resulting from a collision	1 x 10 ⁻¹⁰	CRP1234 Analysis		
Risk of being injured by an HFO-1234yf ignition resulting from a collision	2 x 10 ⁻¹¹	CRP1234 Analysis (updated since VDA mtg.)		
*Rick cited in 1 in 10,000 over the part contury	ļ.	ļ		

*Risk cited is 1 in 10,000 over the next century

Injury sufficiently serious to require hospital visit. Based on number of injuries per year divided by total U.S. adult population.

§ Total number of injuries requiring hospital visit per year divided by the total U.S. population.

** Total number of documented injuries from lightning strikes per year, divided by total U.S. population.

[&] FTA risk multiplied by the number of estimated drivers in the U.S..



 Plant Process Design & Planning 	In progress
✓ Second Species Development test – Preliminary results	Mar 2008
 Development Test - final report 	Aug 2008
 Regulatory: SNAP/ASHRAE filed; REACH to be filed 	Jul 2008
 1-Gen Reproductive test results 	Aug 2008
 Obtain Industry convergence/multiple OEM commitments Industry adoption of HFO-1234yf Firm volumes projections to finalize facility plans (June 2008) 	Sept 2008
Obtain Honeywell/DuPont Capital Commitment/Funding	Oct 2008
Plant Construction end & plant start-up	Nov 2010



Excellent environmental properties

- Very low GWP of 4, Zero ODP, Favorable LCCP
- Atmospheric chemistry determined and published

Low toxicity, similar to R-134a

- Low acute and chronic toxicity
- Significant testing completed

System performance very similar to R-134a

- Excellent COP and Capacity, no glide
 - From both internal tests and OEM tests
- Thermally stable and compatible with R-134a components
- Potential for direct substitution of R-134a

Mild flammability (manageable)

- Flammability properties significantly better than 152a; (MIE, burning velocity, etc)
- Potential for "A2L" ISO 817 classification versus "A2" for 152a based on AIST data
- Potential to use in a direct expansion A/C system better performance, lower weight, smaller size than a secondary loop system



For further information on HFO-1234yf please visit:

www.genetron.com,

www.refrigerants.dupont.com, and

www.SmartAutoAc.com

Thank you!

DISCLAIMER

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