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Update on a Low GWP Refrigerant: Fluid H

Mark W. Spatz
Global Leader Refrigerant Technology
Honeywell Fluorine Products

SAE 2007 Alternatives Refrigerant Systems Symposium
July 17-19, 2007





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Agenda

- Material compatibility
- Stability
- Environmental
- Toxicity
- Performance
- Servicing



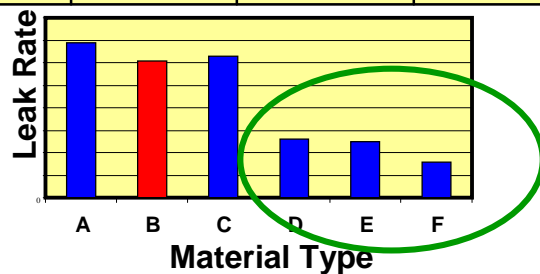
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Compatible Materials are Available

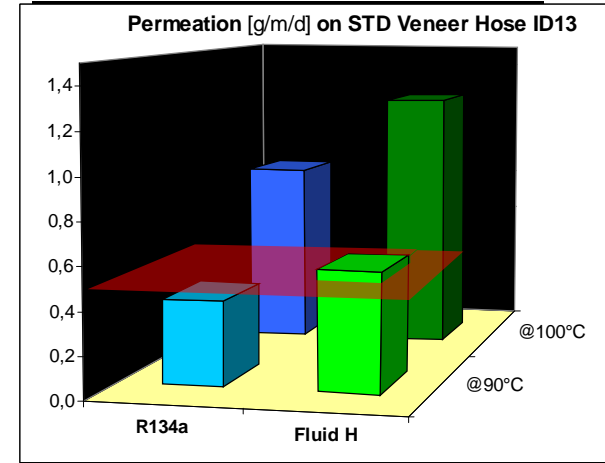
System was mini-shed tested

- Baseline R134a & Drop-in Fluid H
- Acceptable level of leakage and selective permeation obtained using same scaling factor as R-134a.
- The materials and hoses used (type B) was shown by an independent lab to have alternatives with reduced permeation.

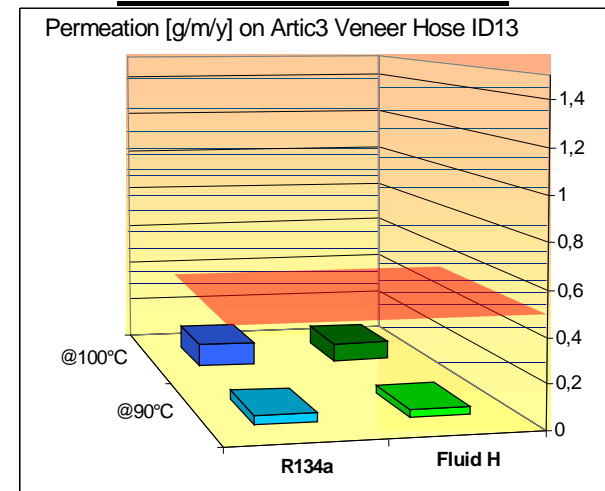
R134a	Fluid	Selective permeation	
		5 years	10 years
Base-line	H	73/27	76/24
10 g/y	15-17g/y		



Standard Veneer Hose



Artic3 Veneer Hose





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Improved Stability Results With POE Lubricants

Significant progress made in optimizing POE formulations for Fluid H.

- **Several lubricant producers have formulated commercial POE lubricants**
 - Pass test at 175 C, 33% saturated water with copper, steel and aluminum
 - Some copper discoloration
- **Other lubricant companies continue to evaluate PAGs, POEs and Alkyl benzene lubricants**
- **Honeywell compressor testing**
 - Fixed displacement compressor passes 400 hour test
 - Variable displacement compressor test recently completed.



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CPI Demonstrated Good Stability with Fluid H

- Sealed Tube: 190°C for 24 hr
 - No visual lubricant change
 - No solids or deposits
 - TAN <2 mg KOH/g
- Sealed Tube: 175°C for 14 days
 - No visual lubricant change
 - No solids or deposits
 - TAN <2 mg KOH/g
- 190C 24hr TAN significantly lower

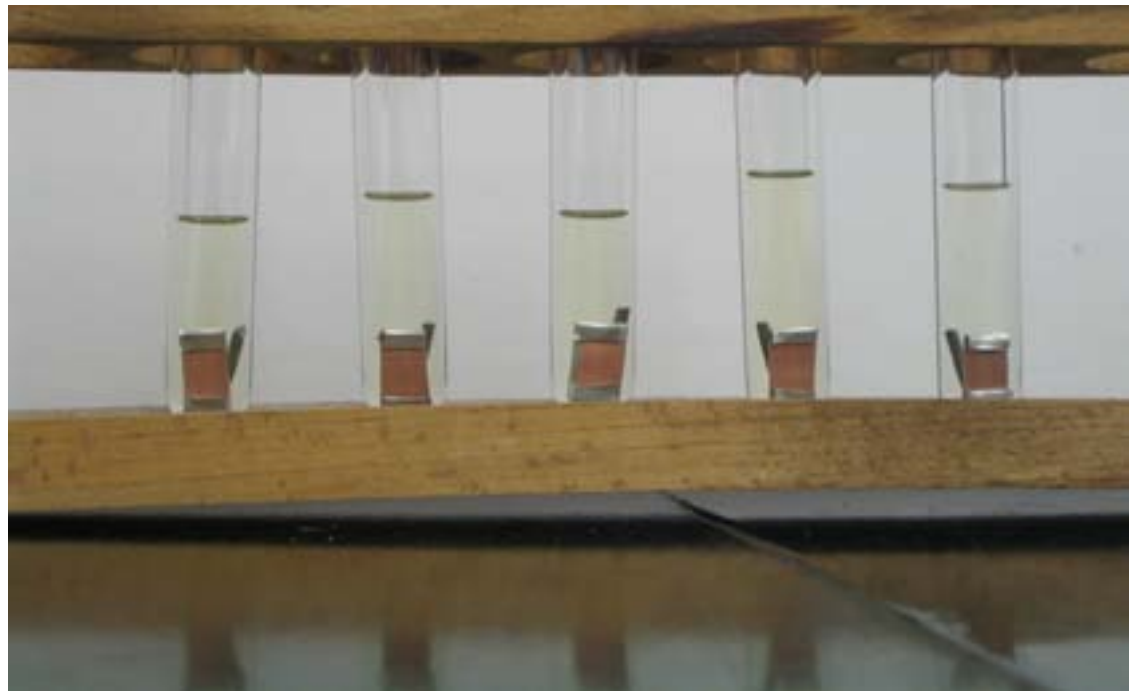


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CPI Results: Sealed tube results at 190°C/24hr

190°C/24 hrs	TAN EOT
Sample 1	2.1
Sample 2	2.2
Sample 3	2.2
Sample 4	1.9
Sample 5	2.3
Sample 6	1.7
Sample 7	1.8
Sample 8	1.4
Sample 9	1.7
Average	1.9
Std Dev	0.3

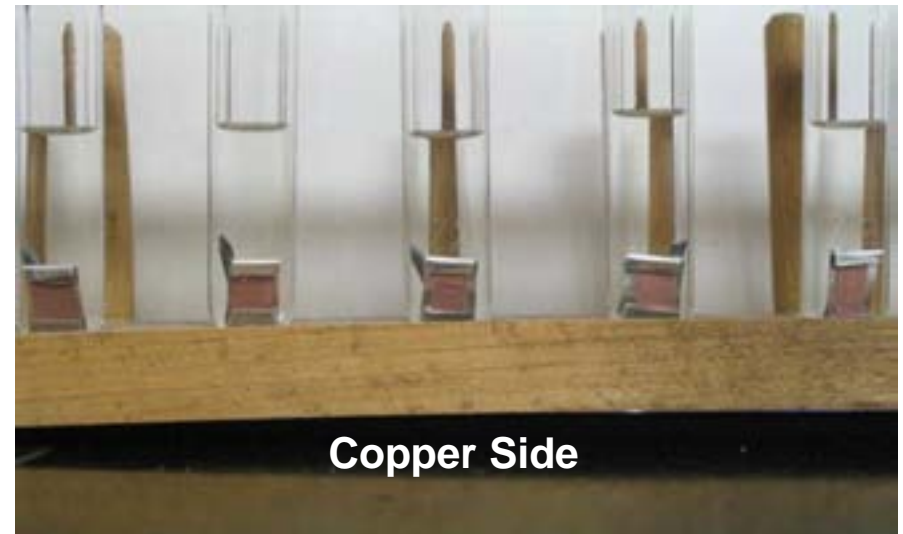
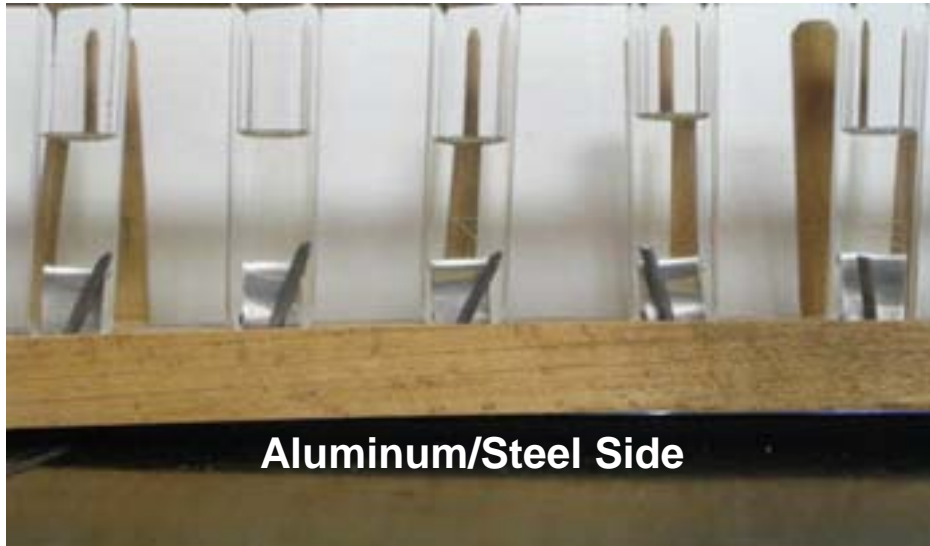




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Sealed tube results at 175°C for 2 weeks





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Additional Stable Oils for Fluid H



- ISO VG 80 POE Thermal Stability
 - Sealed Tube Test 30% Fluid H, Cu, Al, and Fe
 - No Oil Discoloration, No Deposits Observed
- 190°C / 24h 175°C / 2 wks



Water ~35 ppm
 TAN 0.56

~35 ppm
 0.13

Water 300 ppm
 TAN 1.3
 Copper Matt

800ppm
 2.1
 Matt

Encouraging Compressor Test Results with Latest Lubricants

- **Honeywell compressor testing**
 - Low charge, high pressure, heated compressor environment.
 - Fixed displacement compressor passed 400 hour test
 - No unusual wear
 - All parts appeared bright
 - Very low TAN (below 0.2)
 - Visually the oil remained clear (like original).
 - Variable displacement clutchless compressor recently completed same test.
 - No significant change in lubricant chemistry
 - Awaiting tear-down analysis.

Fixed Displacement Compressor



Variable Displacement Compressor





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Favorable Environmental Properties of Fluid H

- **1234yf:**
 - Atmospheric chemistry determined at University of Copenhagen.
 - Atmospheric lifetime is 12 days via reaction with *OH radicals in the atmosphere.
 - Direct $GWP_{100} = 4$.
 - ODP = 0
- **CF₃I:**
 - Atmospheric chemistry previously determined.
 - CF₃I decomposes photolytically.
 - Atmospheric Lifetime is 1-4 days in air, in sunlight.
 - Direct $GWP_{100} \sim 1$.
 - Study to update 2D ODP values and extend to 3D completed.
 - Results for both 2D & 3D = 0.006
 - Applying these values to the blend of 70% 1234yf and 30% CF₃I results in an ODP of 0.002 for Fluid H.
 - The study that developed these values will soon be published.



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Recent Toxicity Update

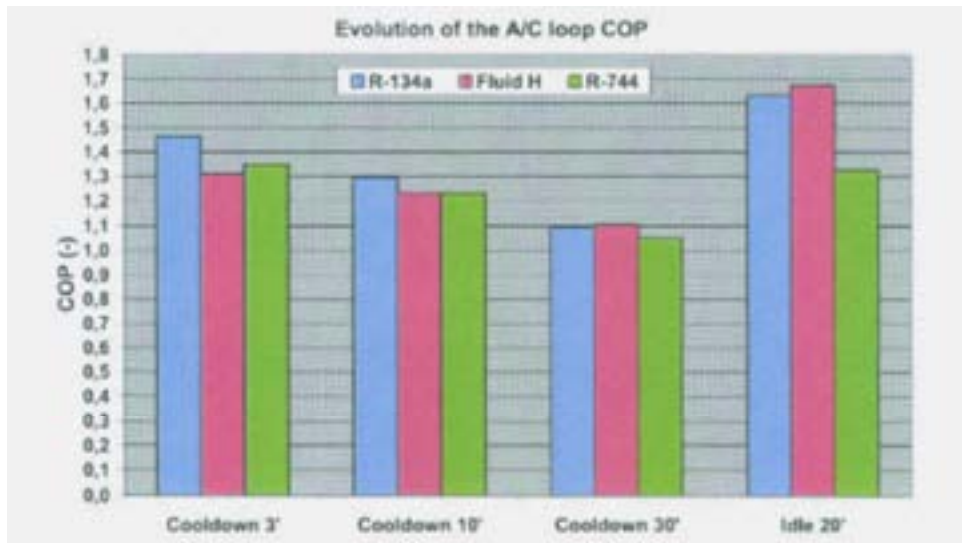
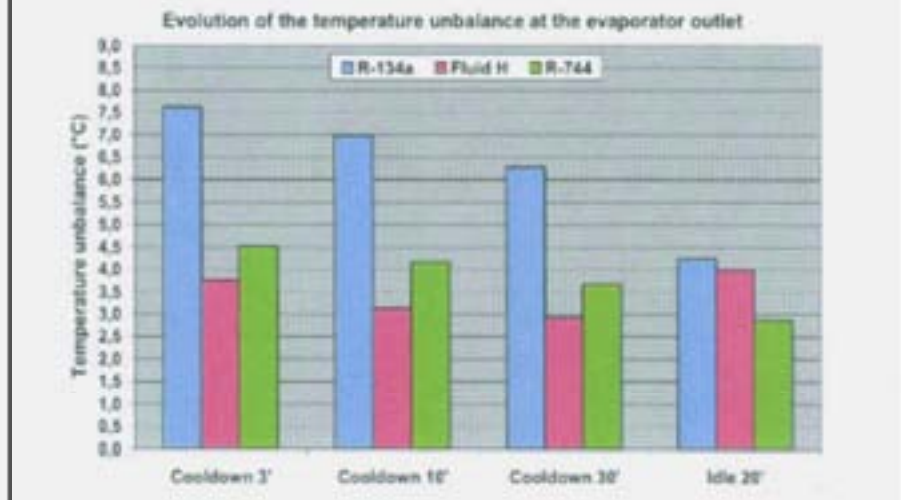
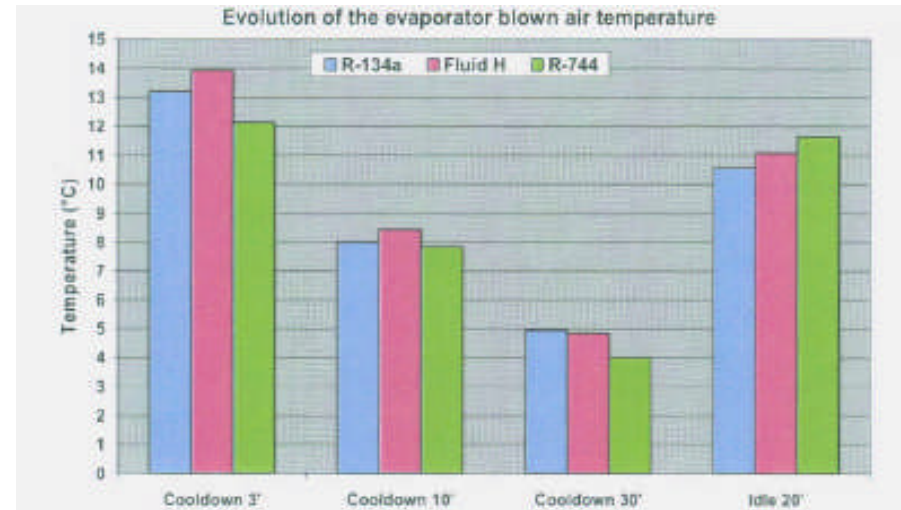
- **1234yf:**
 - **Completed 90 exposure study**
 - **NOEL = 50,000 (highest value tested)**
 - **Completed genomic carcinogenicity test**
 - **Findings: 1234yf non-carcinogenic**
 - **Honeywell AEL established at 1000 ppm (same as R-134a).**
- **CF3I:**
 - **Completed genomic carcinogenicity test**
 - **Findings: CF3I non carcinogenic**



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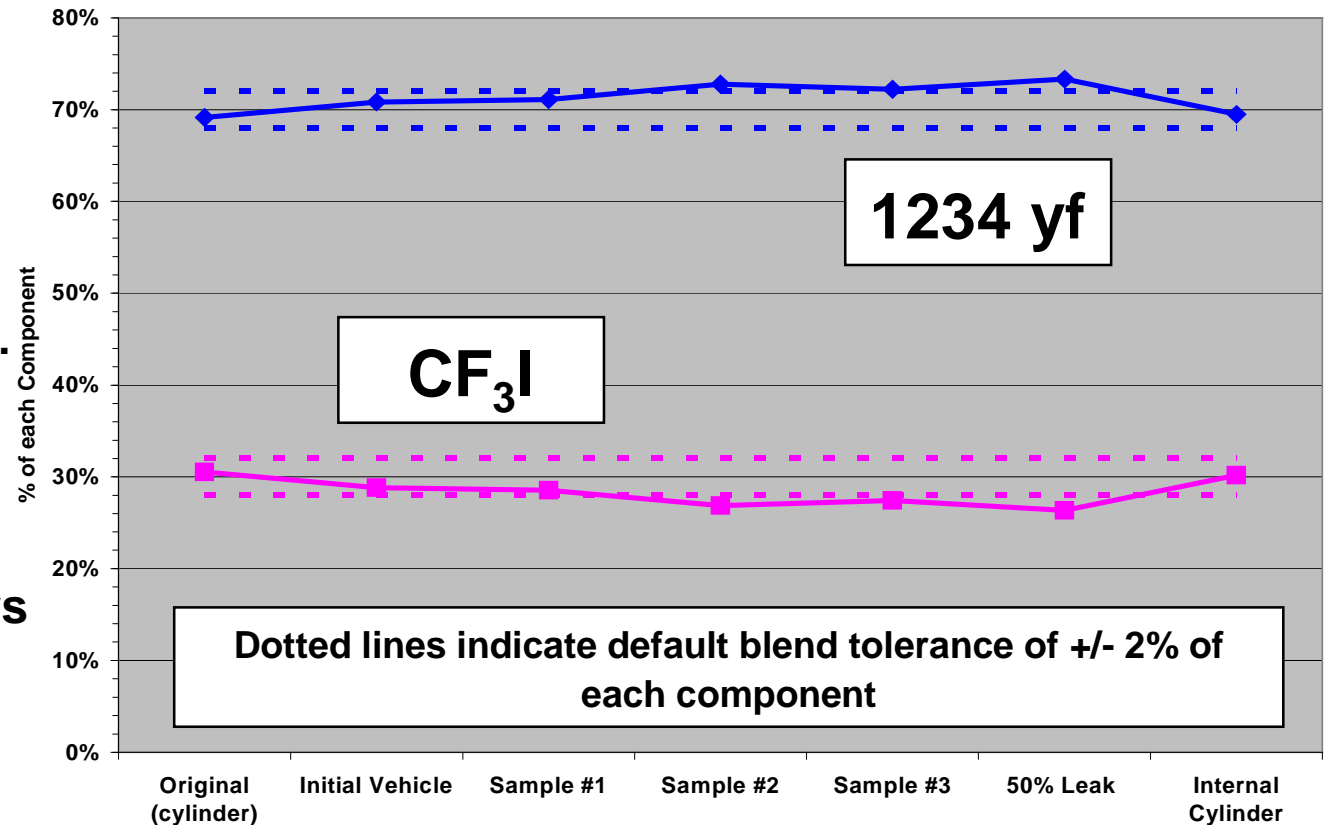
Fluid H Performance

- Results of numerous tests conducted by OEMs and Tier 1's show comparable capacity with minimal hardware change and potential for equivalent COP with optimization.
- Example: Valeo results presented at recent VTMS meeting.



Use Std. Servicing Procedures & Equipment

- Tests performed on standard recycling unit.
 - 3 cycles performed followed by a simulated 50% leak.
 - No change in composition in internal tank.
- R-134a leak detectors can be used.





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Conclusions

- **Significant progress made in the development of this refrigerant.**
- **Stability continues to improve with latest generation lubricants.**
- **Compatible materials are available.**
- **Lower leak rates than 134a production component system demonstrated with next generation seal and hose materials.**
- **Favorable environmental & toxicity results.**
- **Results of performance evaluations are promising especially in optimized systems.**
- **Aftermarket service procedures unchanged from R-134a.**
- **This refrigerant continues to show promise as a cost-effective LGWP replacement for R-134a.**

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DP-1 Update – Low GWP MAC Refrigerant

**Barbara Minor
Engineering Fellow
DuPont Fluoroproducts**

*SAE 2007 Alternatives Refrigerant Systems
Symposium July 17-19, 2007*





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Topics

- Environmental
- Safety
- Compatibility
- DP-1 Optimization
- Industry Performance Testing
- Conclusions



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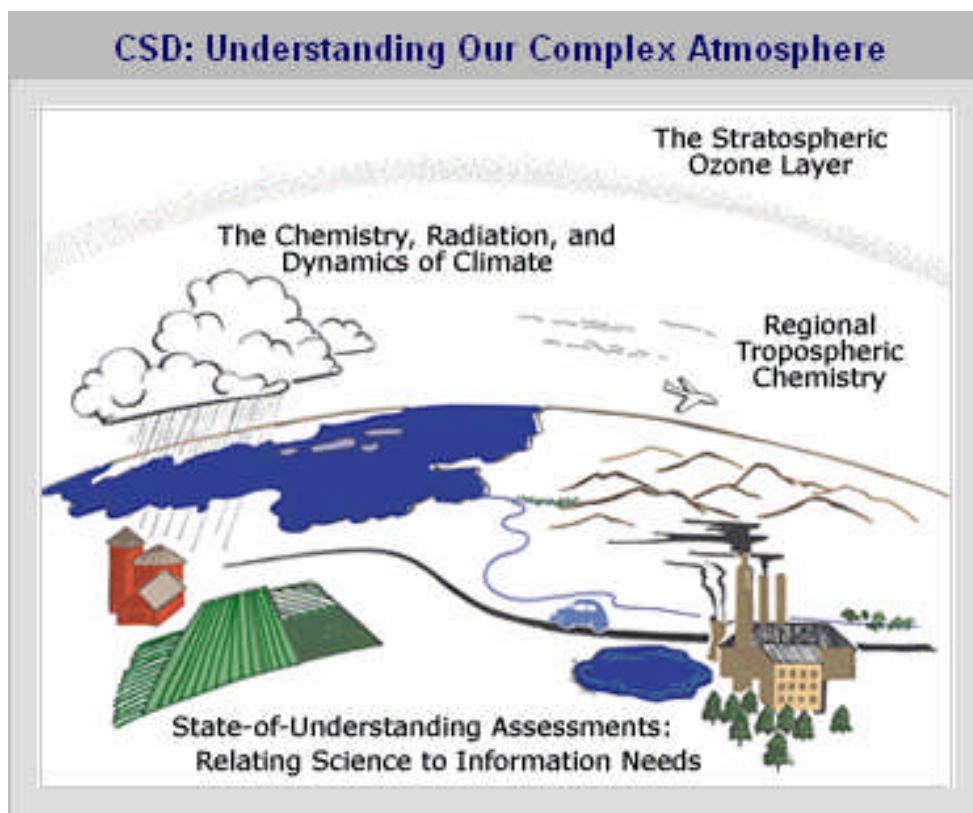
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DP-1: Excellent Environmental/Safety Properties

- Zero-ODP
- Very Low GWP:
 - Estimated at 30-35 (well below EU 150 limit)
 - Provides margin for uncertainty involving future changes in GWP determination (SAR, TAR, SROC)
 - 3rd party measurements in progress; final paper – July/07
- Non-flammable (by ASHRAE Std 34 and ASTM 681 under all required scenarios)
- Improved LCCP versus CO₂ and 134a

Determination of DP-1 GWP and Degradation Products

Work on new compound being conducted at
NOAA Earth System Research Laboratory, Chemical Sciences Division (CSD)
Dr. A.R. Ravishankara, Acting Director



Being carried out by a team with long history of CFC-substitute studies

A. R. Ravishankara

R. K. Talukdar

J. B. Burkholder

V. Padadimitriou

R. Portmann



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Status of NOAA Scientists' Testing of New Compound

- Initial GWP determination is complete
 - Estimated GWP for DP-1 is about 30-35
 - Lifetime of new compound is about 10 days
- Path Forward
 - Further investigation of degradation pathways and products to ensure no “show stoppers”
 - More detailed GWP calculation based on 3-D model results for atmospheric distribution of short lived compounds
 - “Smog chamber” studies to investigate VOC properties
 - Preparation and publication of papers with results from above studies and presentation to EU



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Toxicity Status – New Compound

<u>Test</u>	<u>Status</u>
• Acute - short term (e.g. vehicle driver)	
– 4 hour LC50	
– Ames	
– In vitro chrom ab	
– In vivo micronucleus	
– Cardiac sensitization	
• Repeated dose – long term (e.g. mfr/service)	
– 28 day inhalation	
– 90 day inhalation	
– Developmental/reproductive	

Next steps – Provide data to OEMs for use in their risk assessments; develop mitigation options as needed



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DP-1: Excellent Plastics Compatibility

- Compatible with Apollo ND8 at 100°C for two weeks

Refrigerant	Plastics	Rating	24 h Post Weight Chg. %	Physical Change
DP-1	Polyester	0	4.8	1
"	Nylon	1	-1.3	2
"	Epoxy	1	0.4	2
"	Polyethylene Terephthalate	0	2.7	1
"	Polyimide	0	1.6	1

Refrigerant	Plastics	Rating	24 h Post Weight Chg. %	Physical Change
R134a	Polyester	0	5.6	1
"	Nylon	1	-1.4	2
"	Epoxy	1	0.3	2
"	Polyethylene Terephthalate	0	2.8	1
"	Polyimide	0	0.7	1

Rating 0 = weight gain < 1 and physical change = 0
 1 = weight gain > 1 and < 10 and/or physical change = 2
 2 = weight gain > 10 and/or physical change = 2



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DP-1: Excellent Elastomers Compatibility

- Compatible with Apollo ND8 at 100°C for two weeks

Refrigerant	Elastomers	Rating	24 h Post Linear Swell %	24 h Post Weight Gain %	24 h Post Delta Hardness
DP-1	Neoprene WRT	0	-1.1	-1.0	1
"	HNBR	0	2.0	7.5	-6.5
"	NBR	0	-0.6	0.3	-2.5
"	EPDM	0	-0.5	-0.6	-0.5
"	Silicone	1	0.6	2.1	-9
"	Butyl rubber	0	1.1	-0.2	-4

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
"	Butyl rubber	1	-1.1	-1.6	-3.5

Rating:

- 0 < 10% weight gain and < 10% Linear swell and < 10 hardness change
- 1 > 10% weight gain or > 10% Linear swell or > 10 hardness change
- 2 > 10% weight gain and > 10% Linear swell and > 10 hardness change

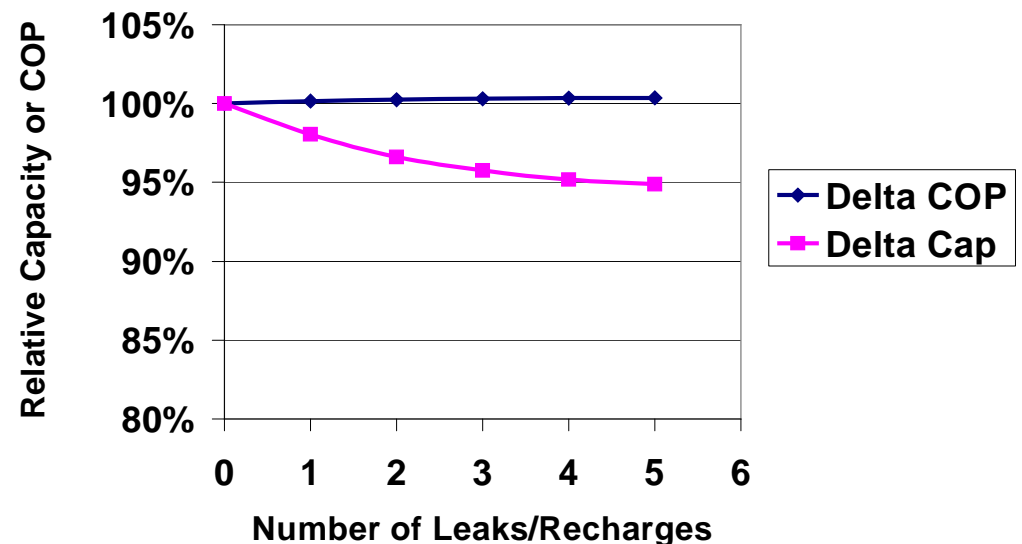


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No Significant Issues with Temperature Glide

- **DP-1 capacity drops only about 5% after multiple leaks and recharges of the system,**
- **COP increases slightly**
- **No performance or design issues due to glide identified during partner testing**

DP-1 Vapor Leak/Recharge From a System

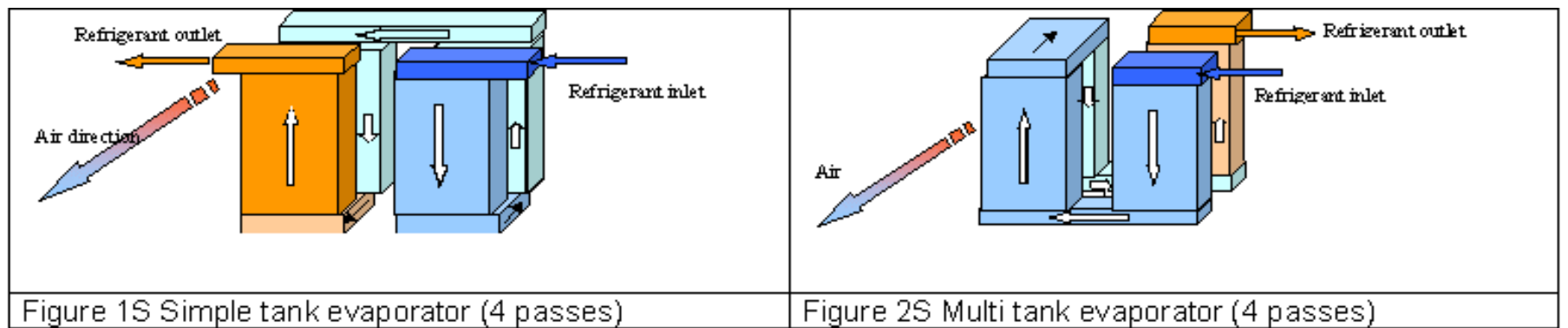


Third Party DP-1 Soft Optimization Recommendations

- Adjust evaporator pressure for DP-1 to about 10% less than R134a (e.g. 270 kPa DP-1 vs 300 kPa R134a).
- For orifice tube, go to next lower diameter size versus R134a, also to achieve lower evaporating pressure
- Target subcooling similar to R134a
 - Increase charge size of DP-1 about 5-10%
 - Because DP-1 discharge pressure is lower than R134a, there is room to increase charge size
- Target superheat similar or slightly less (e.g. 1-2°C) than R134a due to temperature glide

DP-1 Equipment Optimization Options

- Modify evaporator to achieve counter-current flow which can provide an advantage for a glide refrigerant such as DP-1



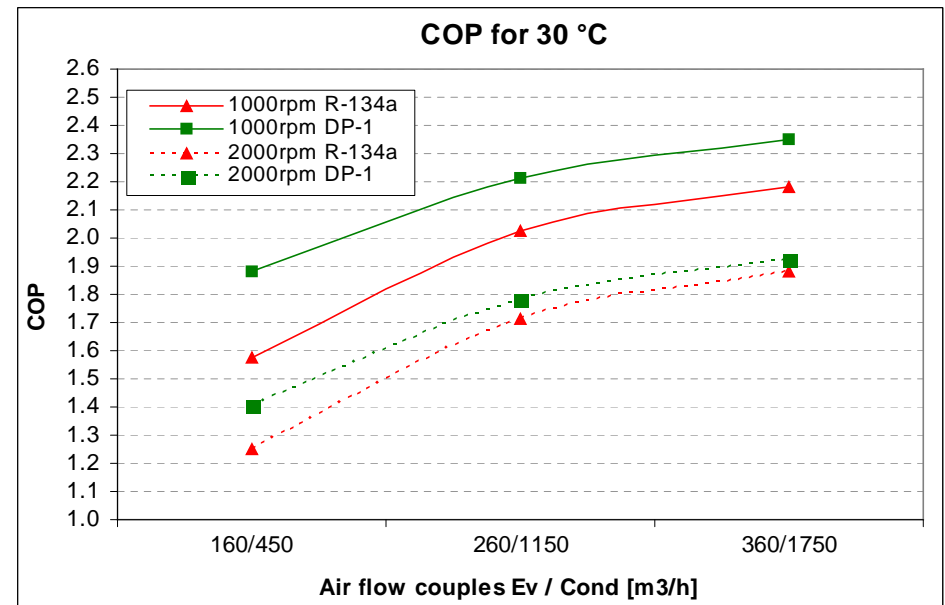
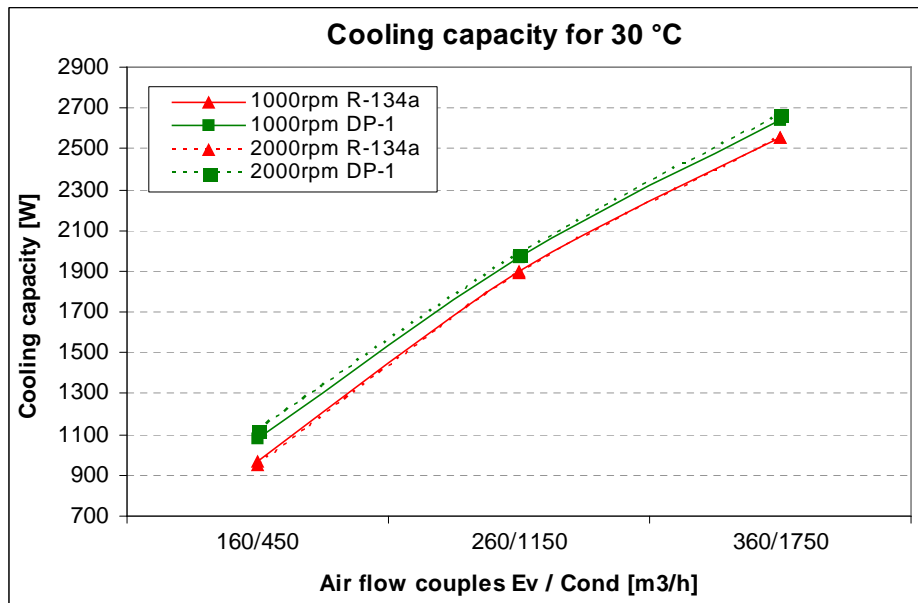
- Optional internal heat exchanger also increased capacity 4-7% and COP 2.5-4% (not used in following tests)



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Cooling Capacity and COP in an Optimized System - 30°C Ambient Temperature



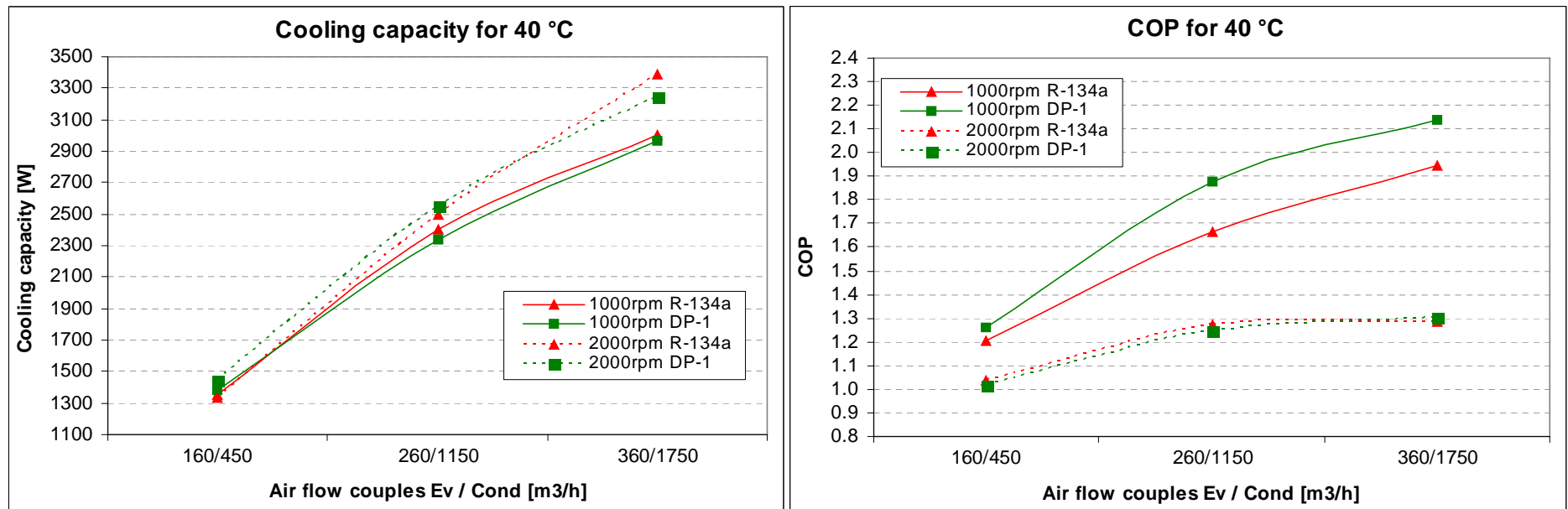
Cooling Capacity Equivalent to R134a and Energy Efficiency 5-10% higher



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Cooling Capacity and COP in an Optimized System – 40°C Ambient Temperature

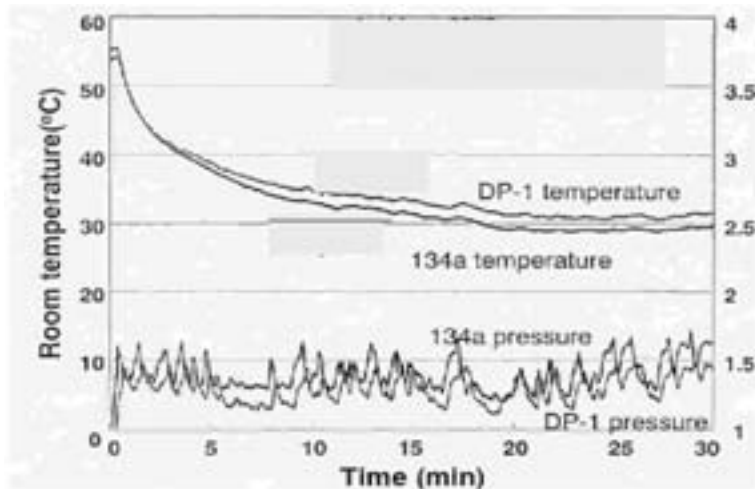


Cooling Capacity Equivalent to R134a and Energy Efficiency 0-10% higher

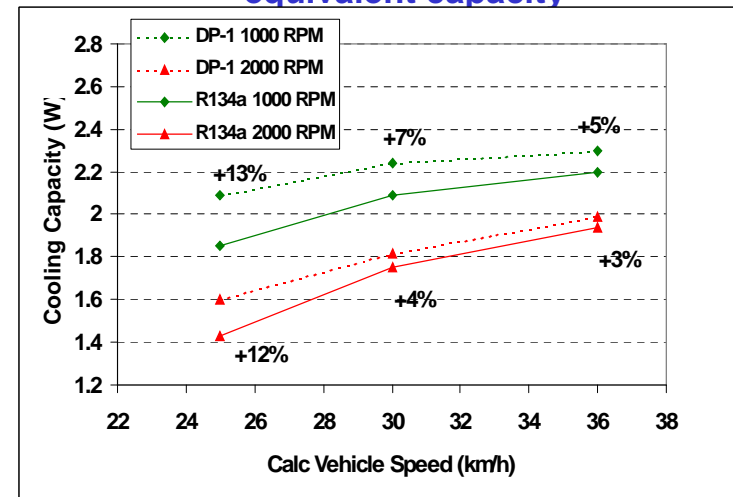
DP-1: Industry Performance Testing

- Industry-wide testing in progress across all regions and levels
- OEM and Tier 1 direct substitution (TXV adj. only) evaluations – very encouraging results
 - Energy efficiency (COP) equivalent or better than R134a
 - Modest capacity deficit of approximately 5-10%
- Significant improvements demonstrated via minor component optimization

DP-1 direct substitution (TXV adj. Only)



DP-1 average COP 5-10% better than R134a at equivalent capacity





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DP-1 Conclusions

- Excellent environmental properties (zero-ODP, very low GWP, low LCCP)
- Low acute toxicity, some repeated dose effects
- Compatible with current R-134a materials
- Cooling capacity similar to R-134a can be achieved with minor component optimization
- Potential for improved energy efficiency versus R-134a
- Significant progress by OEMs and Tier 1s in test evaluations



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Refrigerant JDH – Joint Collaboration Between DuPont and Honeywell

Mark Spatz

Honeywell

Barbara Minor

DuPont

***SAE 2007 Alternatives Refrigerant Systems Symposium
July 17-19, 2007***





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Introduction

- Refrigerant JDH - product of joint Honeywell and DuPont effort.
- Formulated utilizing technology strengths of both companies
- Formulated with existing molecules of Fluid H and DP-1
 - Previous property and performance information can be leveraged



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Refrigerant JDH

- Two component blend
- Excellent environmental properties (zero-ODP, very low GWP, good LCCP)
- Low acute toxicity
- Non-flammable
- Low fractionation (temperature glide = 0.5°C)
- Low hose permeation
- Compatible with current R-134a MAC technology
- Targeted for all climates and all vehicles



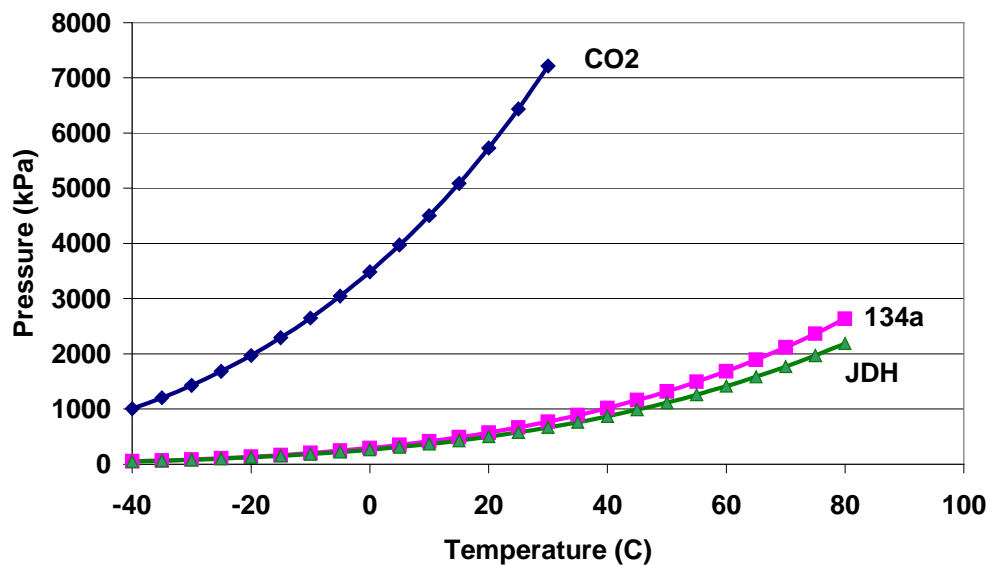
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Refrigerant JDH Properties Provide Better Match for R-134a than CO₂

Property	JDH	R-134a	CO ₂
BP (°C)	-25	-26	-78
Tc (°C)	100	101	31
Pc (kPa)	3282	4059	7377

PT Chart





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Refrigerant JDH – Excellent Environmental Properties

- Zero-ODP
- Very Low GWP:
 - 100 yr experimentally determined to be 4 (well below EU 150 limit)
 - Provides margin for uncertainty involving future changes in GWP determination (SAR, TAR, SROC)
- Improved LCCP versus enhanced CO₂ and enhanced R-134a
 - Planning to perform detailed LCCP calculations based system performance results



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Refrigerant JDH is Non-Flammable

- Multiple conditions are modeled to insure non-flammability in worst case scenarios:
 - Worst case formulation (WCF) at 100°C, 50% RH
 - Worst case fractionated formulation (WCFF) at 60°C, 50% RH
 - 90% full at 54.4°C
 - 90% full at bubble point plus 10°C
 - 90% full at 23°C
 - 15% full at 60°C
 - 15% full at bubble point plus 10°C
- Worst case formulations were confirmed experimentally
- Refrigerant JDH is non-flammable per ASTM-681 and ASHRAE Standard 34

} Simulating leaks from storage containers

} Simulating leaks from equipment



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Refrigerant JDH Toxicity Status

- Acute toxicity testing for the components of Refrigerant JDH are complete with excellent results – JDH has low acute toxicity
- Sub-acute/chronic toxicity tests are in progress for Refrigerant JDH – Initial results expected 3-4Q'07

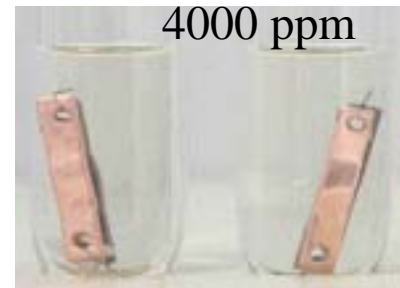
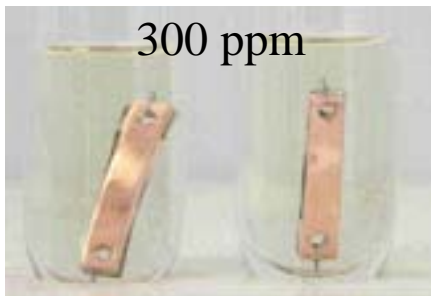


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Refrigerant JDH has Excellent Thermal Stability

Refrigerant JDH and Nippon GS10 PAG 175°C, 2 weeks



Temp	Time	Moisture	TAN
175	2 weeks	300	1.3 ± 0.1
175	2 weeks	4000	2.1 ± 0.1



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Thermal Stability - Continued

Refrigerant JDH with ND8 175°C for 2 weeks

300 ppm water



4000 ppm water



Temp	Time	Moisture	TAN
175	2 weeks	300	1.9 ± 0.1
175	2 weeks	4000	2.4 ± 0.2

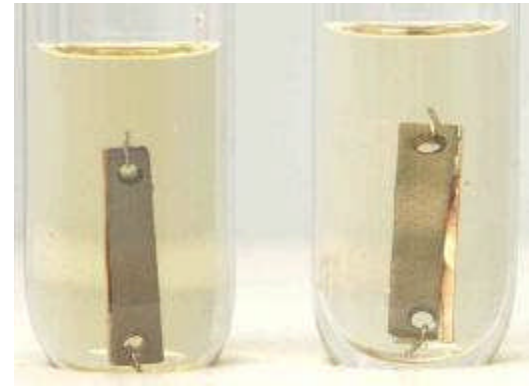


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Thermal Stability - Continued

Refrigerant JDH and Nippon POE 13 190°C 14 days



Temp °C	Time	Moisture	TAN
190	14 day	50	0.07±0.01

Good Stability even at 190°C for two weeks.
This is an extremely severe test.



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Refrigerant JDH: Excellent Plastics Compatibility Apollo ND8 PAG at 100°C for two weeks

Refrigerant	Plastics	Rating	24 h Post Weight Chg. %	Physical Change
JDH	Polyester	0	4.4	1
"	Nylon	0	-0.9	1
"	Epoxy	0	0.2	1
"	Polyethylene Terephthalate	1	2.4	1
"	Polyimide	0	0.6	1

Refrigerant	Plastics	Rating	24 h Post Weight Chg. %	Physical Change
R134a	Polyester	0	5.6	1
"	Nylon	1	-1.4	2
"	Epoxy	1	0.3	2
"	Polyethylene Terephthalate	0	2.8	1
"	Polyimide	0	0.7	1

Rating 0 = weight gain < 1 and physical change = 0
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 2 = weight gain > 10 and/or physical change = 2



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Refrigerant JDH: Excellent Elastomers Compatibility- Apollo 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
JDH	Neoprene WRT	0	0.1	-0.5	-1.5
"	HNBR	0	0.9	6.3	-3
"	NBR	0	-1.4	-0.6	0.5
"	EPDM	0	-1.3	-1.2	0
"	Silicone	1	0.1	2.9	-10
"	Butyl rubber	0	-1.4	-2.0	-5

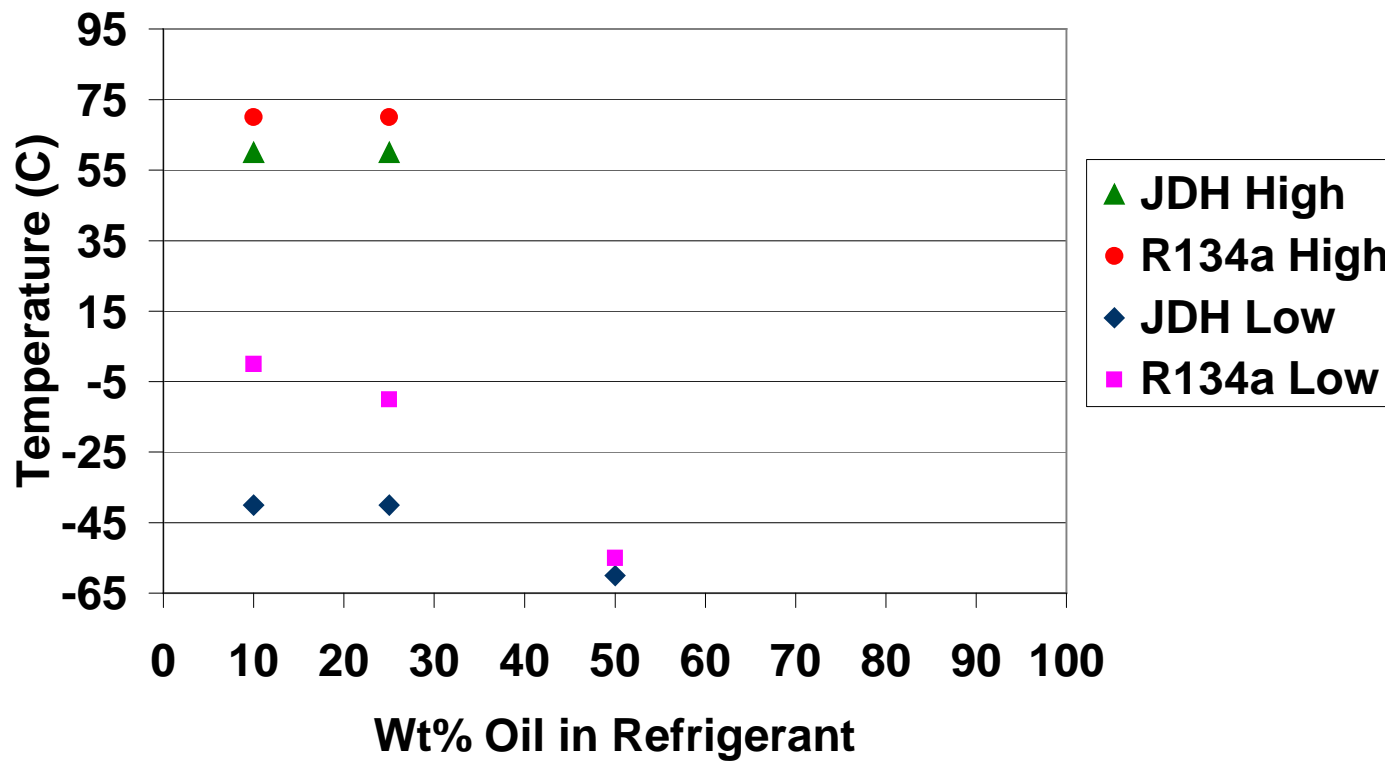
Refrigerant	Elastomers	Rating	24 h Post Linear Swell %	24 h Post Weight Gain %	24 h Post Delta Hardness
R134a	Neoprene WRT	0	-0.6	-1.3	2
"	HNBR	0	2.1	8.6	-5.5
"	NBR	0	0.0	3.0	-3.5
"	EPDM	0	-1.1	-0.4	-2
"	Silicone	0	-1.4	1.4	-2.5
"	Butyl rubber	1	-1.1	-1.6	-3.5

Rating:

- 0 < 10% weight gain and < 10% Linear swell and < 10 hardness change
- 1 > 10% weight gain or > 10% Linear swell or > 10 hardness change
- 2 > 10% weight gain and > 10% Linear swell and > 10 hardness change

Refrigerant JDH: Excellent Miscibility with PAG Lubricant

R134a and JDH Miscibility with Apollo PAG



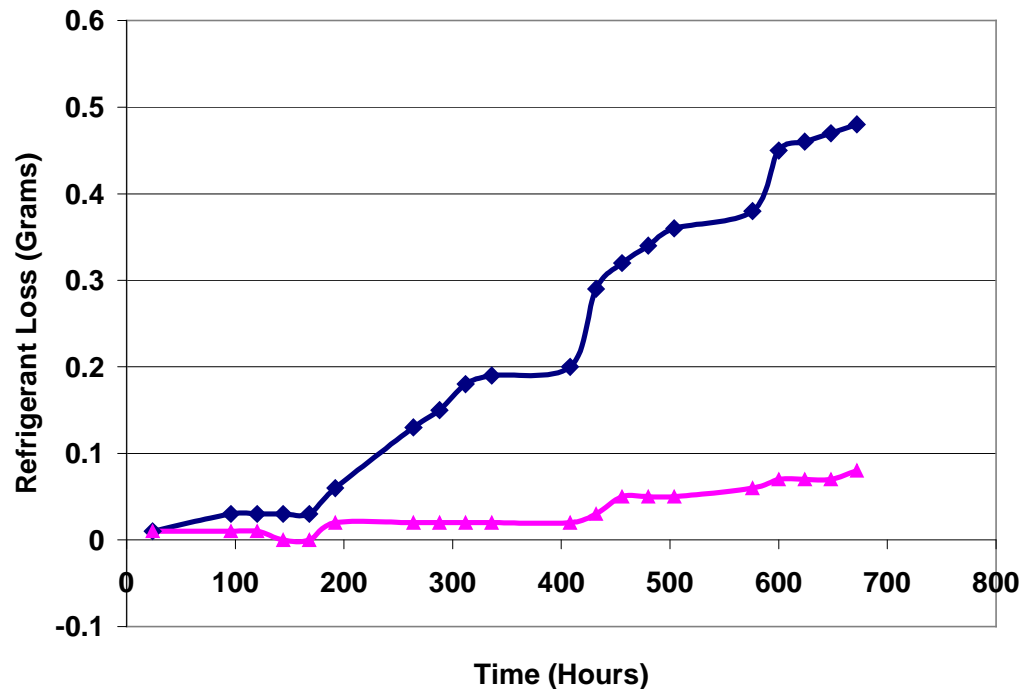
Refrigerant JDH - Low Hose Permeation

-Test conducted with low permeation hose for R-134a and near JDH formulation at 80C for 28 days (SAE Std J2064):

Leak Rate: R134a 0.45 kg/m²/yr

JDH 0.07 kg/m²/yr

Hose Permeation Test - Refrigerant Loss Rate





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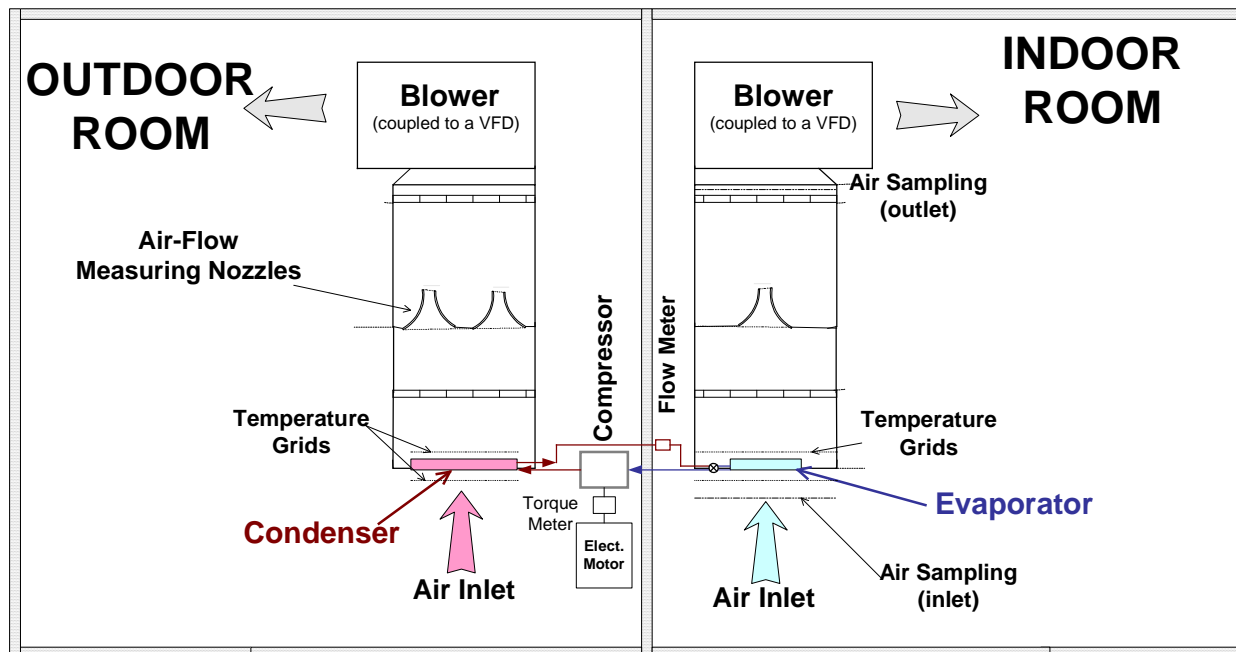
Comparable Thermodynamic Cycle Performance

- The performance of JDH was calculated using thermodynamic properties
- The following typical a/c conditions were utilized:
 - 5°C Evaporator Temperature.
 - 50°C Condenser Temperature.
 - 5°K Superheat & Subcooling.
 - 70% Compressor Isentropic Efficiency.

	Evaporator Pressure kPa	Condenser Pressure kPa	Discharge Temp. °C	Temp. Glide °C	Capacity kJ/m ³	COP	Relative Capacity	Relative COP	Relative Mass Flow
R-134a	350	1318	70	0	2373	3.5	100%	100%	100%
Refrigerant JDH	320	1147	59	0.5	1958	3.4	83%	97%	112%

System Performance Bench Test Facility

- Wind tunnels constructed to test automotive a/c system similar to SAE testing.
- System tested: Opel Astra a/c system manufactured by Delphi.
- Measurements made:
 - Refrigerant circuit:
 - Temp. and pressure at inlet & outlet of all major components.
 - Mass flow.
 - Compressor torque and rpm
 - Air side:
 - DB temperature distribution in/out of evaporator and condenser.
 - Dew point in/out of evaporator.





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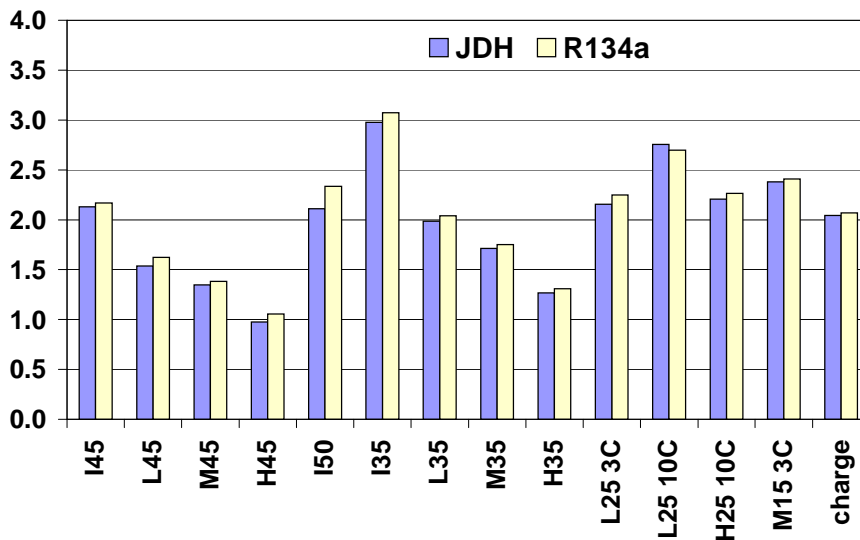
Industry Common Test Points Selected

Test Name	Ambient temp.	Compressor Speed	Condenser Temp. Face Velocity [m/s]		Evaporator				Targeted air temp. downstream of evaporator
					Typical vehicle			Simulated air selection	
					Temp.	Humidity	Mass flow [kg/min]		
I60	45	900	60	1.5	35	25	9.0	RECIRC	3
I45	45	900	45	1.5	35	25	9.0	RECIRC	3
L45	45	1800	45	2.0	35	25	9.0	RECIRC	3
M45	45	2500	45	3.0	35	25	9.0	RECIRC	3
H45	45	4000	45	4.0	35	25	9.0	RECIRC	3
I50a	35	900	50	1.5	35	40	9.0	OSA	3
I35a	35	900	35	1.5	35	40	9.0	OSA	3
L35a	35	1800	35	2.0	35	40	9.0	OSA	3
M35a	35	2500	35	3.0	35	40	9.0	OSA	3
H35a	35	4000	35	4.0	35	40	9.0	OSA	3
I40c	25	900	40	1.5	25	50	6.5	OSA	3/10
I40a	25	900	40	1.5	25	80	6.5	OSA	3/10
I25a	25	900	25	1.5	25	80	6.5	OSA	3/10
L25a	25	1800	25	2.0	25	80	6.5	OSA	3/10
M25a	25	2500	25	3.0	25	80	6.5	OSA	3/10
H25a	25	4000	25	4.0	25	80	6.5	OSA	3/10
I30	15	900	30	1.5	15	80	6.5	OSA	3/10
I15	15	900	15	1.5	15	80	6.5	OSA	3/10
L15	15	1800	15	2.0	15	80	6.5	OSA	3/10
M15	15	2500	15	3.0	15	80	6.5	OSA	3/10
H15	15	4000	15	4.0	15	80	6.5	OSA	3/10
charge		2000	40	4	40	40			

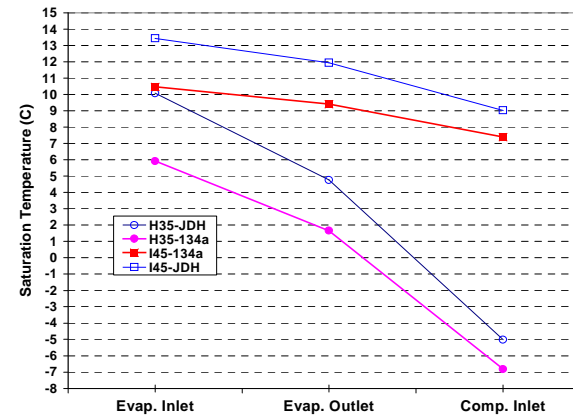
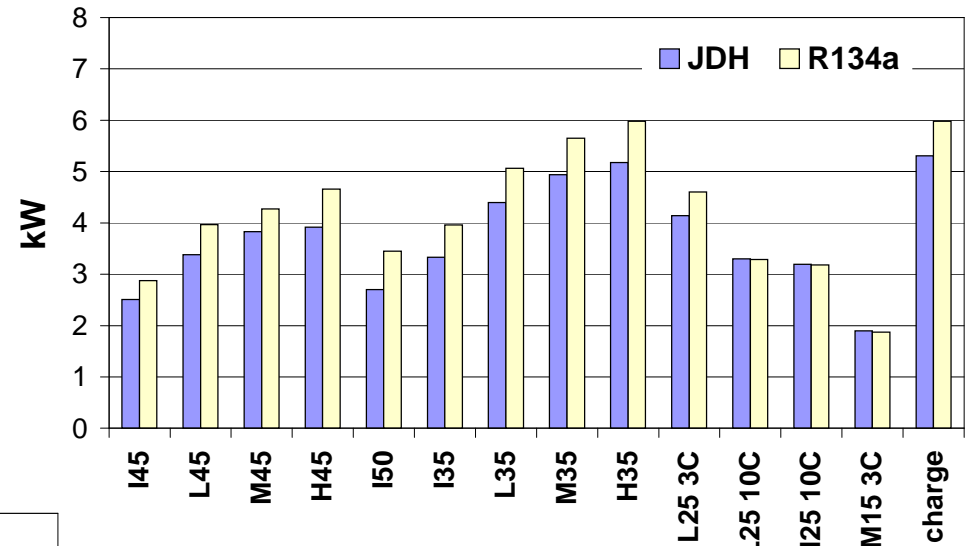
Results of Drop-in Tests

- Refrigerant JDH Performance:
 - Capacity: 85 to 90% of R-134a.
 - COP: 93 to 98% of R-134a.
- No changes were made to system including TXV.
- Improvements likely with minor changes (e.g. lower ΔP suction line).

COP



Capacity

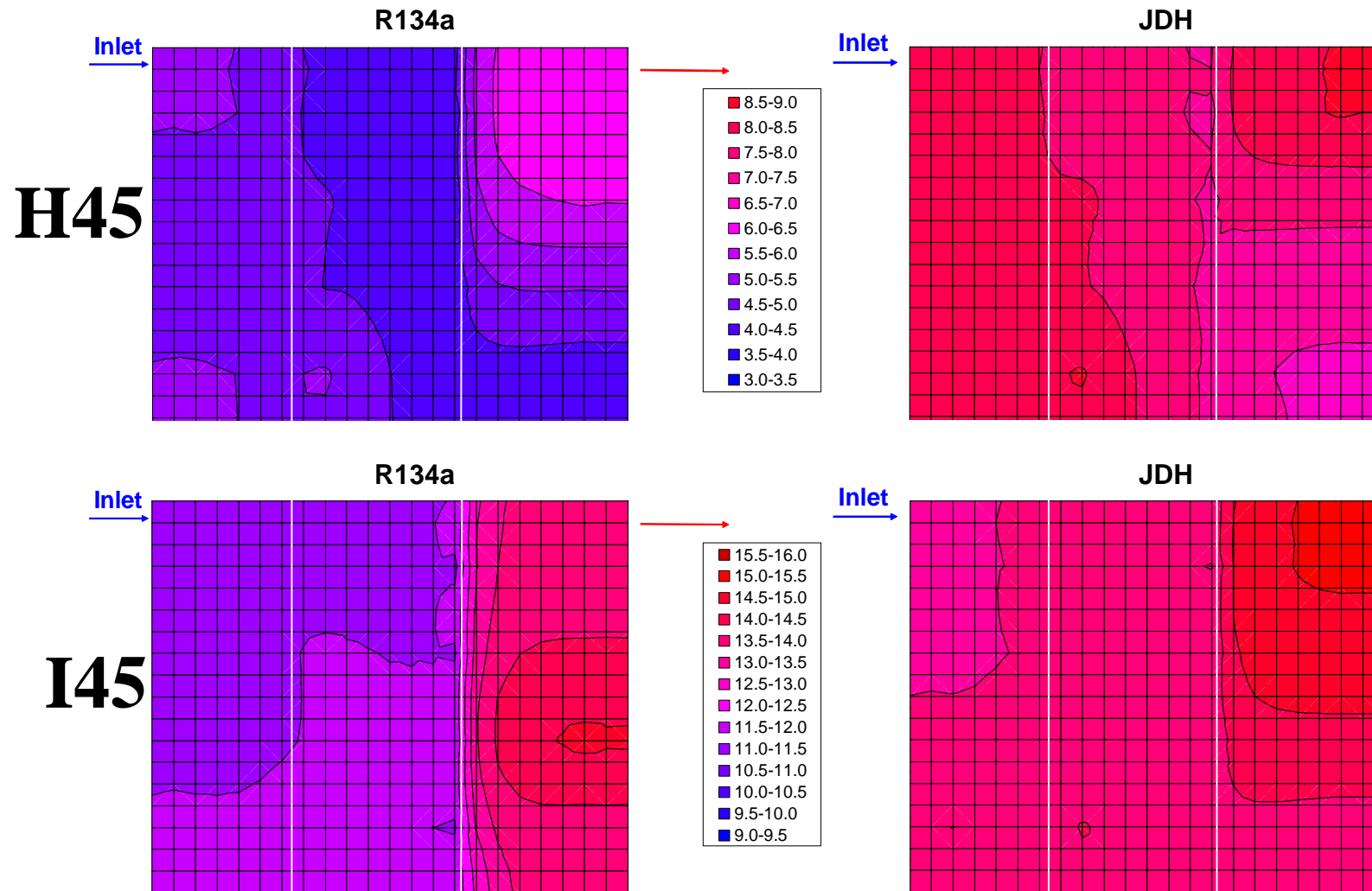




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Uniform Evaporator Outlet Air Temperature Profile at Low & High Flow Conditions





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Refrigerant JDH Can Utilize Standard Recycling Procedures & Equipment

- Tests were performed using a production Robinair 34788 recovery/recycling unit intended for R-134a.
- Testing Sequence:
 - Internal cylinder charged with 7 kg. of Refrigerant JDH.
 - Standard charging procedure utilized.
 - Vehicle run for one hour then shut-down for 24 or more hours.
 - Slow vapor leak (50% by mass) simulated.
 - The above three steps were repeated five times.
 - Samples collected from internal cylinder and vehicle after each recharge.
 - The refrigerant collected in the cylinder after each vapor leak was also analyzed.
- Results: No significant change in the composition. Only a 1% change in composition within the recycling unit's cylinder.





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Refrigerant JDH

- Excellent environmental properties (zero-ODP, very low GWP, good LCCP)
- Low acute toxicity, repeated dose tests in progress
- Non-flammable
- Low fractionation (temperature glide = 0.5°C)
- Low hose permeation
- Compatible with current R-134a MAC technology
- Targeted for all climates and all vehicles



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Path Forward

- Provide data to OEMs for DP-1, Fluid H and Refrigerant JDH for use in their risk assessments
- Identify mitigation options to address any potential issues, as have been developed for CO₂
- Support system, component, and vehicle testing per OEM guidance
- Secure OEM forecasted demand for future EU conversion
- Converge to best candidate based on industry feedback
- Support global convergence to one solution

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