Automotive Material Investigation with Low GWP Refrigerant HFO-1234yf

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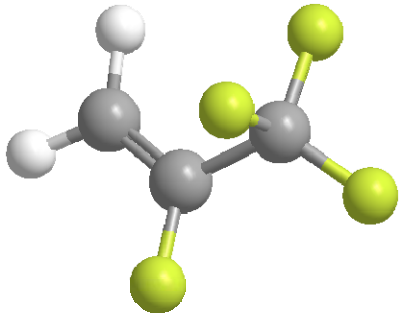
Agenda

- HFO-1234yf
- HFO-1234yf Properties
- Thermodynamic Properties
- HFO-1234yf Flammability Comparison
- Previous Studies
- Thermal Stability
- Material Compatibility
- Summary

HFO-1234yf



HFO-1234yf or Hydrofluoro- olefin

2,3,3,3,-tetrafluoroprop-1-ene ($CF_3CF=CH_2$)

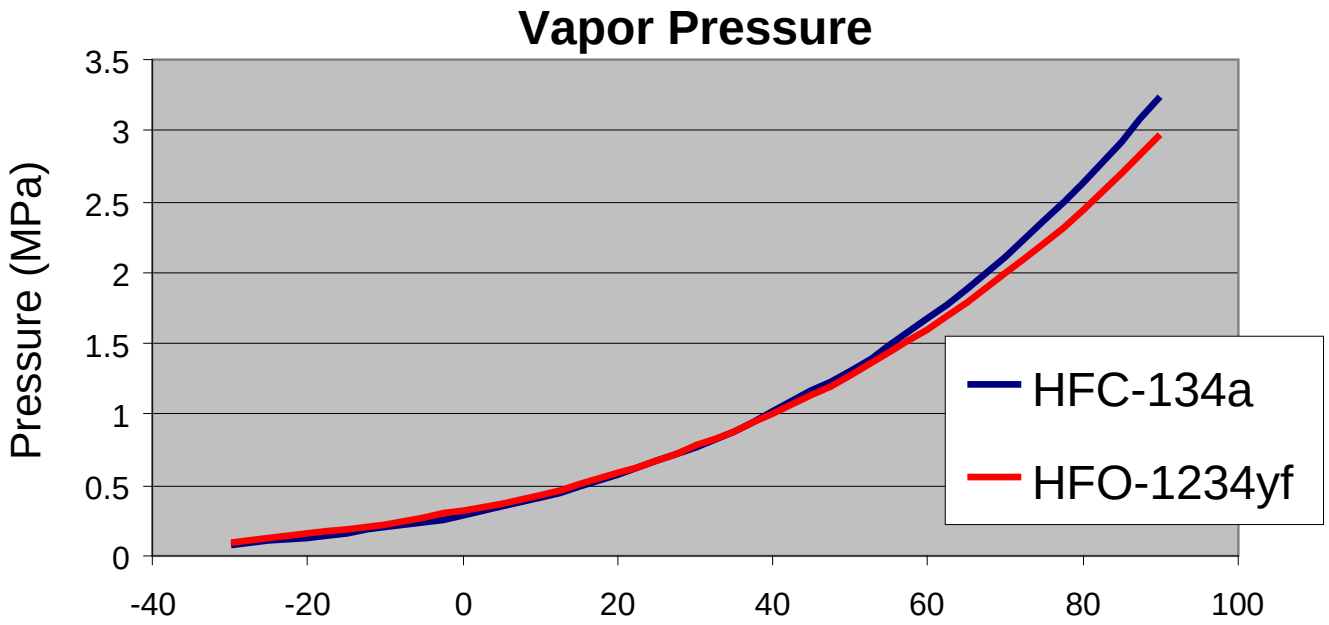
Refrigerant Which Offers Balance Of Properties And Performance

- Excellent Environmental Properties, GWP = 4, Zero ODP
- Comparable To 134a For Refrigeration Properties
- Acceptable Stability And Compatibility Properties

Mildly Flammable (But **Significantly Less** So Than HFC-152a and R32)

HFO-1234yf Properties

Properties	HFO-1234yf	HFC-134a
Pvap, MPa (25°C)	0.677	0.665
Pvap, MPa (80°C)	2.44	2.63
GWP (100 ITH)	4	1430 (AR4)
Toxicity	A-Low	A-Low
Flammability	Mild	None

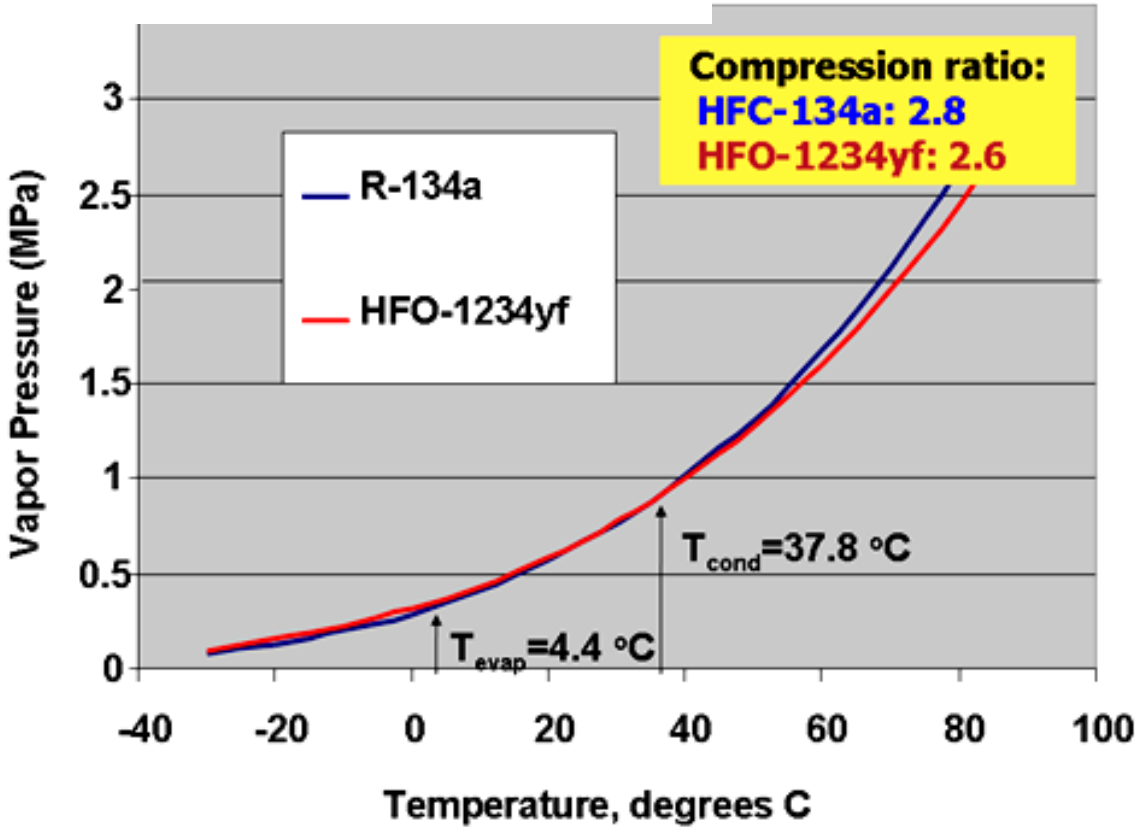


- Same operating conditions as 134a (similar P/T curve)
- Thermally stable under extreme use conditions in a MAC system
- Cooling capacity equivalent to 134a
- Energy efficiency better or equivalent to 134a
- Only modest design changes required in MAC

HFO-1234yf has vapor pressure, toxicity class A, similar to R-134a, but has mild flammability

Thermodynamic Properties

Properties	HFO-1234yf	HFC-134a
Boiling Point, T_b	-29°C	-26°C
Critical Point, T_c	95°C	102°C
P_{vap}, MPa (25°C)	0.677	0.665
P_{vap}, MPa (80°C)	2.44	2.63
Liquid Density, kg/m^3 (25°C)	1094	1207
Vapor Density, kg/m^3 (25°C)	37.6	32.4



Flammability Comparison

		HFC-134a	HFO-1234yf	HFC-152a	Propane	Gasoline	Hydrogen	Ethanol**
Flame Limits- ASTM E681-01 at 21C								
	LFL (vol% in Air)	N/A	6.2	3.9	2.2	1.4	4	3.3
	UFL (vol% in Air)	N/A	12.3	16.9	10	7.6	75	19.0
Minimum Ignition Energy -MIE (mJ)		N/A	>5000	0.38	0.25	0.29	0.016	0.65
Heat of Combustion (kJ/g)		4.2	10.7	16.5	46.3	47	142.9	29.8
Burning Velocity (cm/s)		N/A	1.5	23	46	34	265-325	58
Flammability Index-Low value preferred								
	R	N/A	0.97	1.78	1.99			
	F	N/A	0.27	0.5	0.55	0.57	0.77	0.58
	RF	N/A	3.6	16.6	56.7	62.8		41.7
	RF2	N/A	0.6	17.9	37.2			
* Severy, et. Al.								
** Brandes and Ural								

HFO-1234yf flammability characteristics are "milder than" those of hydrocarbon gases or other commonly used products within the service repair shop.

Previous Material Compatibility Studies

- **HFO-1234yf has been fully evaluated with traditional automotive A/C pieces**
- **Work done by wide array of industry groups**
  - Global OEM's, Tier 1/Tier 2 Automotive Industry Suppliers
    - JAMA-JAPIA
    - SAE Cooperative Research Project (**CRP1234-2)**
- **Some selected previous information shown on next slides**

Material Evaluation Results (1234yf)

Thermal Stability Test

ANSI/ASHRAE97-1999

PAG
PAG1:Serial PAG for MACs
PAG2:PAG (without extreme pressure additive ,oiliness additive)

POE
POE1:Serial POE for HV AC
POE2:Serial POE for Stationary AC

Proposed Spec <3.3

Ref.		R134a				1234yf			
Oil		PAG1	PAG2	POE1	POE2	PAG1	PAG2	POE1	POE2
Condition		175deg-C/14days							
Low Moisture	ppm	<10							
Total Acid Number	mgKOH/g	0.03	0.00	0.00	0.00	1.40	0.06	0.01	0.05
Low Moisture	ppm	1000							
Total Acid Number	mgKOH/g	0.82	0.00	0.01	0.10	2.44	0.17	0.01	1.18
High Moisture	ppm	10000							
Total Acid Number	mgKOH/g	1.75	0.00	21.3	21.4	3.04	0.90	19.5	21.1
Condition		200deg-C/14days							
Low Moisture	ppm	<10							
Total Acid Number	mgKOH/g	1.28	0.00	0.00	0.00	2.88	1.12	0.00	0.06
Low Moisture	ppm	1000							
Total Acid Number	mgKOH/g	1.15	0.54	0.1	0.21	3.49	1.40	2.00	2.84
High Moisture	ppm	10000							
Total Acid Number	mgKOH/g	2.19	0.87	21.4	22.3	3.22	2.05	20.2	21.2

Ref:JAMA-JAPIA 2008 VDA Winter Meeting

Differences in PAG additive package potential to influence TAN, acid number
Several PAG lubricant suppliers have optimized PAG's for HFO-1234yf use

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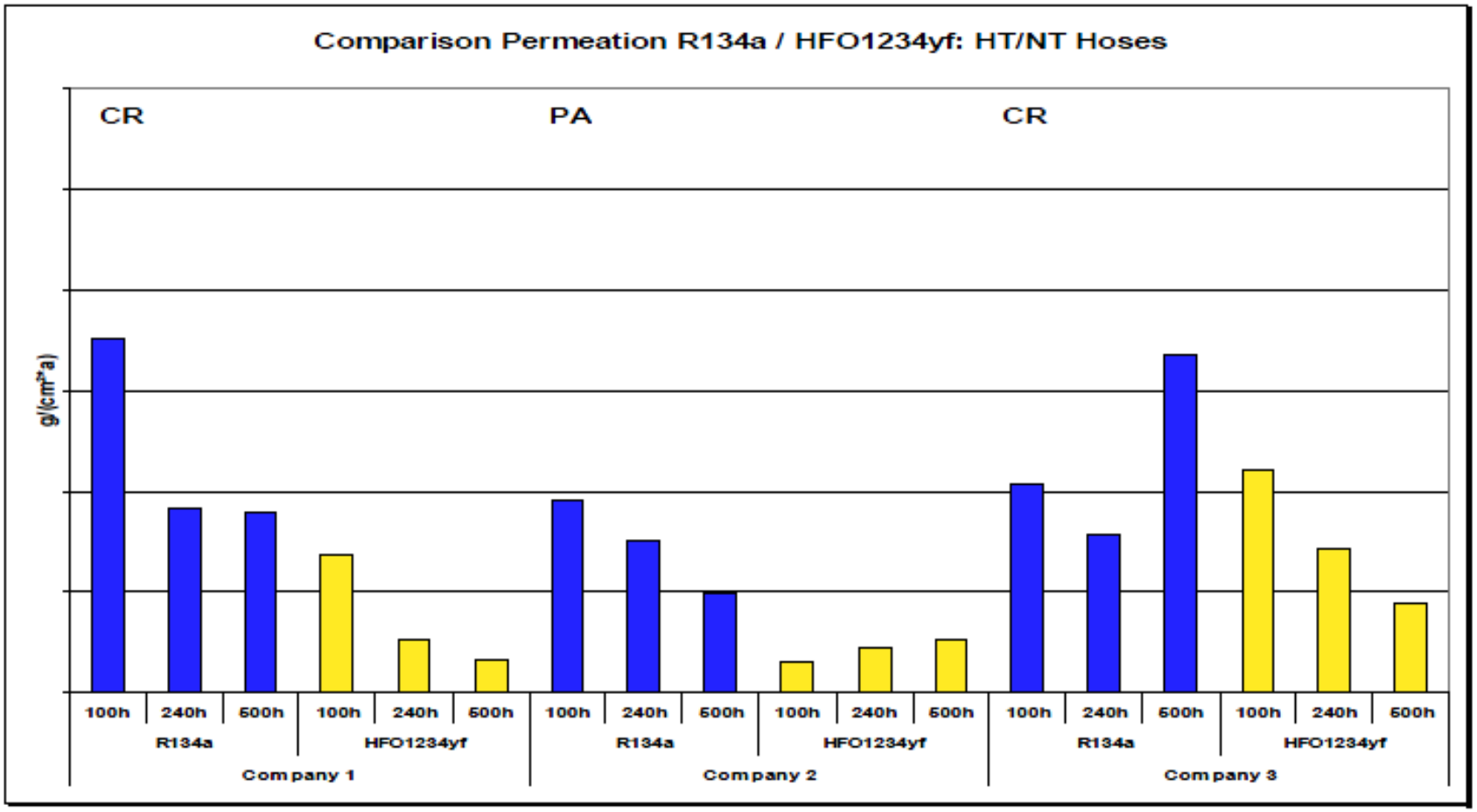
SAE CRP1234-2 Select Permeation Results



In general, for materials tested, HFO-1234yf has lower permeation rates

Ref: Grimm 2008 SAE AARS Phoenix 2008

Previous Material Compatibility Studies

Material	Compatibility			Permeation	Permeation
	PAG Oil A HFO-1234yf	PAG Oil B HFO-1234yf	PAG Oil A R-134a	HFO-1234yf	R-134a
Seals					
EPDM					
EPDM					
EPDM					
EPDM					
HNBR					
HNBR					
HNBR					
CR					
Normal Temp Hoses					
CR					
CIIR					
CR					
CIIR					
PA					
PA					
High Temp Hoses					
CR					
CR					
IIR					
PA					
PA					
PA					
Thermo-plastics					
PPS1					
PPS2					
PEI					

ILK Dresden

Institut für Luft- und Kältetechnik gemeinnützige Gesellschaft mbH

Ref: 2009 SAE CRP1234-2 Report

Green color indicates no issues were noted, Yellow color indicates some improvements are suggested, no color indicates materials were not tested

In all cases, some combination of commercially available material compatible with HFO-1234yf

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HFO-1234yf/PAG Plastics Compatibility

ND8 PAG at 100°C for two weeks

Refrigerant	Plastics	Rating	24 h Post Weight Chg. %	Physical Change
HFO-1234yf	Polyester	1	4.4	0
"	Nylon	1	-1.5	1
"	Epoxy	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
"	Epoxy	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

HFO-1234yf/PAG 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
HFO-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
"	Butyl rubber	0	-1.1	-1.6	-3.5

Rating

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

Additional Compatibility Information

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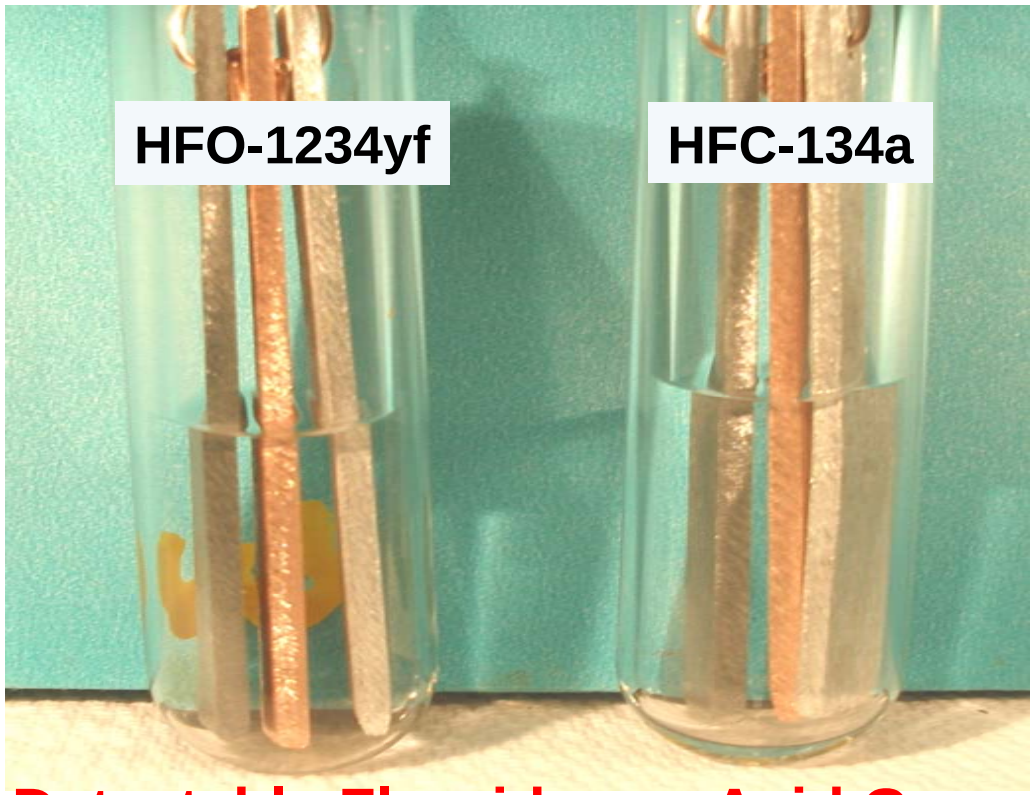
HFO-1234yf Thermal Stability I

Rapidly decomposing in the atmosphere
But stable under service conditions!

Neat HFO-1234yf vs Neat HFC-134a
After 2 wks @ 200 ºC

Sealed tube testing based on ASHRAE-ANSI STD 97



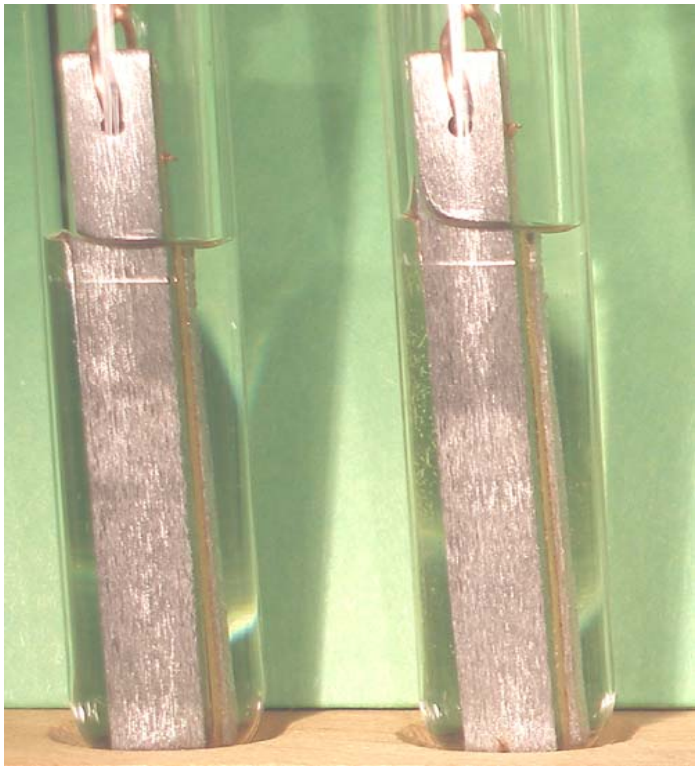
No Detectable Fluoride nor Acid Generation

HFO-1234yf Thermal Stability II

HFO-1234yf / POE vs HFC-134a / POE

AFTER TWO WEEKS @ 175 °C

Front View



HFO-1234yf **HFC-134a**

Side View

HFO-1234yf **HFC-134a**

No Detectable Fluoride nor Acid Generation

DuPont tested multiple POE's and found good thermal stability/miscibility in systems tested

Compatibility with Additional Plastics

% weight change after 2 wks @ 100ºC in HFO-1234yf vs HFC-134a

Polymer	Immediately after exposure		24 Hrs after exposure	
	HFC-134a	HFO-1234yf	HFC-134a	HFO-1234yf
Polyester Resin	7.6	4.2	2.2	2.3
Nylon Resin	0.3	-0.2	-0.5	-0.4
Epoxy Resin	0.1	-0.1	-0.3	-0.1
Polyester PET	9.3	5.3	5.8	3.8
Polyester PBT	12.5	1.1	12.3	1.1
Polycarbonate	4.2	0.9	3.9	0.8
Polyimide	3.7	3.4	3.2	3.2
Polyethylene	1.3	1.7	1.1	1.3
PTFE	2.7	3.0	2.3	2.4
FEP	3.1	3.8	2.7	3.2
ETFE	6.0	4.9	4.8	4.2
Phenolic Resin	-0.8	-0.8	-1.0	-0.8
Acetal Resin	2.7	0.7	2.1	0.6
PET Film	0.8	-1.0	-1.3	-2.1

Compatibility with Additional Elastomers

% weight change after 2 wks @ 100ºC in HFO-1234yf vs HFC-134a

Elastomer	Immediately after exposure		24 Hrs after exposure	
	HFC-134a	HFO-1234yf	HFC-134a	HFO-1234yf
Neoprene WRT	2.6	2.4	1.3	1.3
HNBR	15.2	5.2	9.9	4.4
NBR	14.1	5.8	8.0	4.6
EPDM (Nordel)	3.6	3.5	0.7	0.6
Silicone	10.6	2.0	-0.1	-0.4
Butyl Rubber	4.1	5.0	3.2	4.1
Terminal seal	2.2	4.8	0.8	2.0
Buna S (SBR)	2.7	2.1	1.1	0.8
Viton	47.4	20.0	8.0	8.0
Hypalon	3.2	2.7	2.6	2.4
Neoprene o-ring	-0.4	3.0	-0.5	2.3

Overall: Comparable degree of interaction of polymers & elastomers with 1234yf and 134a

Miscibility ISO 120 POE: HFO-1234yf vs. R-134a

120 cSt Branched Acid POE Lubricant

Refrigerant: HFO 1234yf							Temperature				(C)																		
Lubricant: ISO120 Branched Acid POE																													
% POE	-50	-45	-40	-35	-30	-25	-20	-15	-10	-5	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90
5%	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
10%	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	N	N
15%	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	N	N	N
20%	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	N	N	N
30%	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	N	N	N
60%	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
70%	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
Refrigerant: HFC-134a																													
Lubricant: ISO120 Branched Acid POE							Temperature				(C)																		
% POE	-50	-45	-40	-35	-30	-25	-20	-15	-10	-5	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90
5%	N	N	N	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
10%	N	N	N	N	N	N	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
15%	N	N	N	N	N	N	N	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
20%	N	N	N	N	N	N	N	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
30%	N	N	N	N	N	N	N	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
60%	N	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
70%	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M

HFO-1234yf has larger miscibility range

Miscibility ISO 68 POE: HFO-1234yf vs. R-134a

68 cSt Mixed Acid POE

Refrigerant: HFO 1234yf																														
Lubricant: ISO 68 Mixed Acid POE							Temperature				(C)																			
% POE	-50	-45	-40	-35	-30	-25	-20	-15	-10	-5	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90
5%	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	N
10%	N	N	N	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	N	N	N	N
15%	N	N	N	N	N	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	N	N	N	N	N
20%	N	N	N	N	N	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	N	N	N	N	N	N
30%	N	N	N	N	N	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	N	N	N	N	N	N
60%	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
70%	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
Refrigerant: HFC-134a																														
Lubricant: ISO 68 Mixed Acid POE							Temperature				(C)																			
% POE	-50	-45	-40	-35	-30	-25	-20	-15	-10	-5	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90
5%	N	N	N	N	N	N	N	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
10%	N	N	N	N	N	N	N	N	N	N	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
15%	N	N	N	N	N	N	N	N	N	N	N	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	N
20%	N	N	N	N	N	N	N	N	N	N	N	N	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	N
30%	N	N	N	N	N	N	N	N	N	N	N	N	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	N
60%	N	N	N	N	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
70%	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M

HFO-1234yf has larger miscibility range

Summary

Over last four plus years, HFO-1234yf has been thoroughly investigated by the Automotive Industry

Previous DuPont Material Compatibility/Thermal Stability results indicate good performance with common automotive materials

JAMA and SAE CRP1234-2 results indicate good compatibility/thermal stability with various commercially available common automotive materials

Summary

The next phase of HFO-1234yf product testing will concentrate on understanding the potential to leverage HFO-1234yf for use in electric and hybrid vehicles.

In this investigation, material compatibility with POE lubricants, electric motor materials, and related automotive components were evaluated.

Test results indicate:

- HFO-1234yf is thermally stable even at high temperatures (200°C)
- HFO-1234yf/POE lubricants found to stable at temperatures (175°C).
- HFO-1234yf is slightly less aggressive these materials than HFC-134a, indicating potential for use of HFO-1234yf with electric and hybrid vehicles.
- HFO-1234yf is more miscible with POE lubricants than HFC-134a indicating suitability for use in electric and hybrid vehicles.

More information can be found at:
www.Refrigerants.DuPont.com
www.SmartAutoAC.com

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Thank You !