# Countdown to R1234yf Industry Preparation

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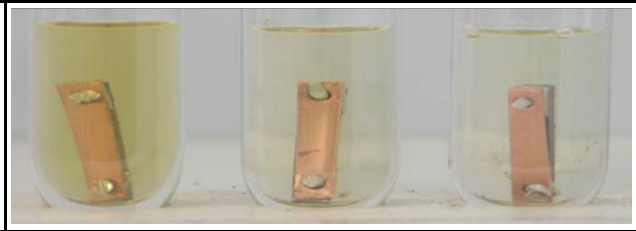
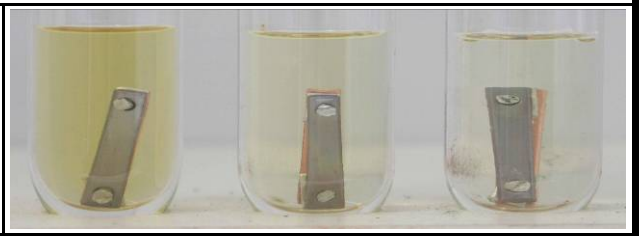
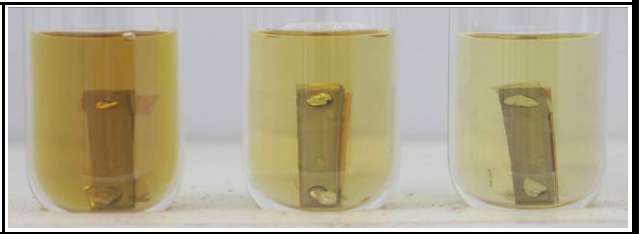
# Outline

- **Lubricant – Refrigerant Compatibility**
  - **Past sealed tube results**
  - **New sealed tube results**
  - **Vehicle Durability Results**
- **HFO-1234yf Purity for SAE J2844**
- **Dealing with R-134a Contamination of HFO-1234yf Systems**
- **Recent Events**

# HFO-1234yf Thermal Stability, 14 Days
# R134a PAG 1

| Lubricant | | PAG 1 (copper side) | | | PAG 1 (Steel side) | | |
|---|---|---|---|---|---|---|---|
| Moisture | ppm | <100 | 1000 | 10000 | <100 | 1000 | 10000 |
| Temperature, °C | | 175 °C | | | | | |
| Photograph | |  | | |  | | |
| Color / Wt. Change % | | Yellow | Light yellow | V. Light Yellow | -0.00 | +0.01 | +0.13 |
| Sludge / Fluoride (ppm) | | Not Present | Not Present | Not Present | 74 | 29 | 25 |
| Total Acid Number (mg KOH/g) | | 1.65 | 2.11 | 2.55 | | | |
| Temperature, °C | | 200 °C | | | | | |
| Photograph | |  | | |  | | |
| Color / Wt. Change % | | Yellow | Light yellow | Light Yellow | +0.01 | +0.03 | +0.13 |
| Sludge / Fluoride (ppm) | | Not Present | Not Present | Not Present | 129 | 75 | 42 |
| Total Acid Number (mg KOH/g) | | 2.36 | 2.55 | 2.51 | | | |

**HFO-1234yf Accelerated Stability Test with a Commercial PAG Lubricant:**
**TAN Slightly Higher than R-134a, Slightly Higher Color, Fluoride Levels**

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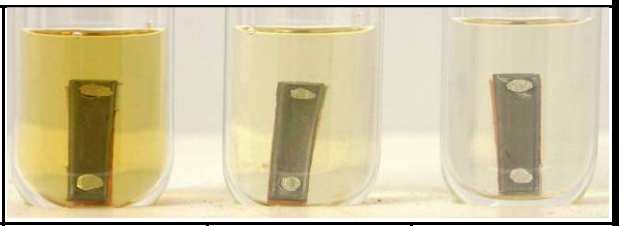
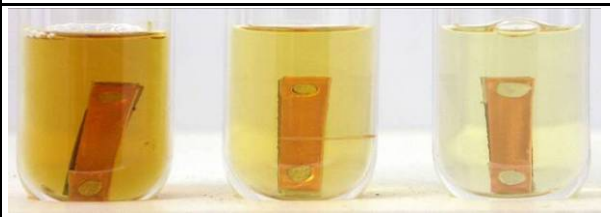
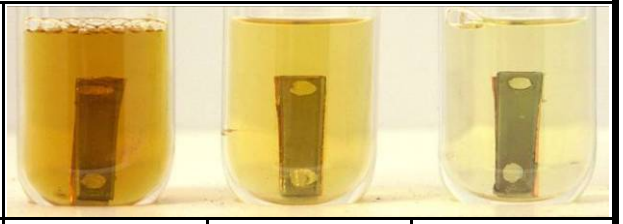
# HFO-1234yf Thermal Stability, 14 Days
# R134a PAG 2

| Lubricant | | PAG 2 (copper side) | | | PAG 2 (Steel side) | | |
|---|---|---|---|---|---|---|---|
| Moisture | ppm | <100 | 1000 | 10000 | <100 | 1000 | 10000 |
| Temperature, °C | | 175 °C | | | | | |
| Photograph | |  | | |  | | |
| Color / Wt. Change % | | Slightly Yellow | Clear | Clear | NA | 0.03 | 0.23 |
| Sludge / Fluoride (ppm) | | Not Present | Not Present | Not Present | 98 | 66 | 10 |
| Total Acid Number (mg KOH/g) | | 1.48 | 2.05 | 1.61 | | - | - |
| Temperature, °C | | 200 °C | | | | | |
| Photograph | |  | | |  | | |
| Color / Wt. Change % | | Yellow | Slightly yellow | Slightly yellow | 0.02 | 0.05 | 0.25 |
| Sludge / Fluoride (ppm) | | Not Present | Not Present | Not Present | 118 | 68 | 38 |
| Total Acid Number (mg KOH/g) | | 2.15 | 2.23 | 1.44 | - | - | - |

**HFO-1234yf Accelerated Stability Test with a Commercial PAG Lubricant**
**TAN Slightly Higher than R-134a, Slightly Higher Color, Fluoride Levels**

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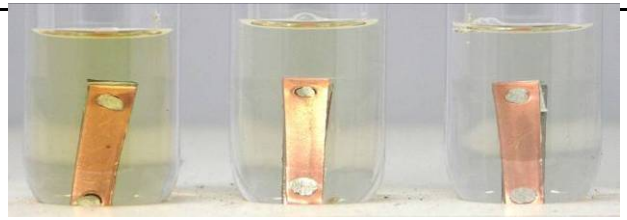
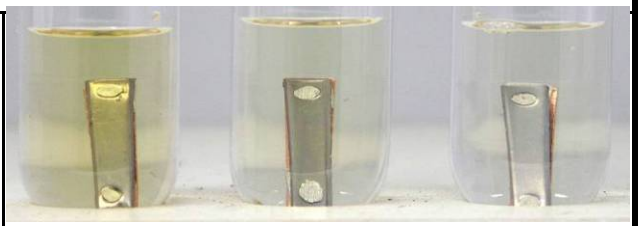
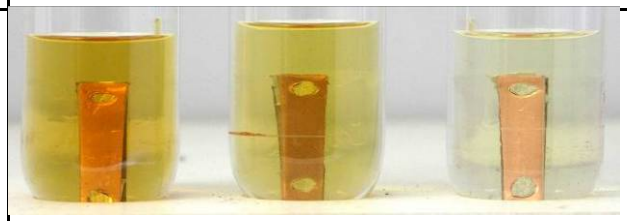
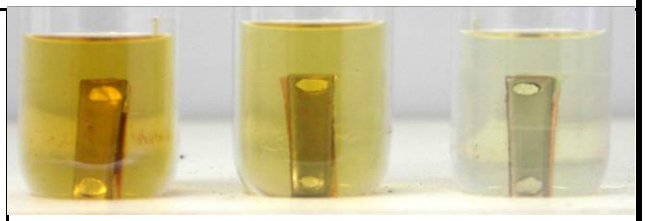
# HFO-1234yf Thermal Stability, 14 Days
# R134a PAG 2 With 6 mmHg Air

| Lubricant | | PAG 2 (copper side) | | | PAG 2 (Steel side) | | |
|---|---|---|---|---|---|---|---|
| Moisture | ppm | <100 | 1000 | 10000 | <100 | 1000 | 10000 |
| Temperature, °C | | 175 °C | | | | | |
| Photograph | |  | | |  | | |
| Color/wt. change % | | Yellow | Light yellow | V. Light Yellow | 0.01 | 0.02 | 0.10 |
| Sludge/Fluoride (ppm) | | Not Present | Not Present | Not Present | <0.1 | <0.1 | 13 |
| Total Acid Number (mgKOH/g) | | 2.9 | 2.2 | 2.4 | | | |
| Temperature, °C | | 200 °C | | | | | |
| Photograph | |  | | |  | | |
| Color/wt. change % | | Yellow | Yellow | Light Yellow | 0.020 | 0.03 | 0.15 |
| Sludge/Fluoride (ppm) | | Not Present | Not Present | Not Present | 89 | 64 | 28 |
| Total Acid Number (mgKOH/g) | | 2.3 | 2.4 | 2.2 | | | |

**Lighter Color, Lower Fluoride Suggest Oil Additive Interaction With Air Different**

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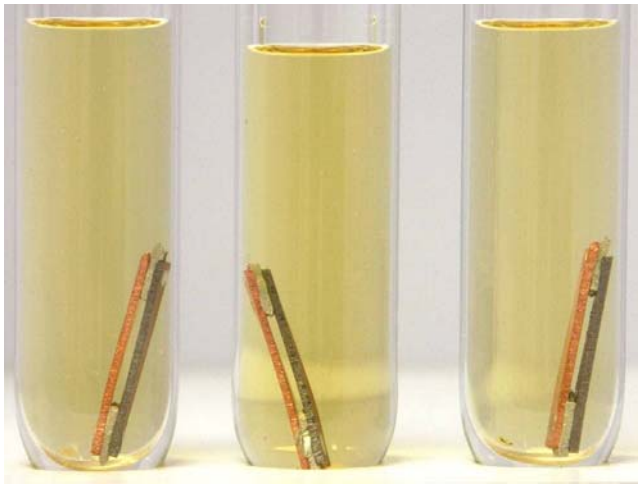
# HFO-1234yf with 0.1% HFO-1234ze



HFO-1234yf with 0.1% HFO-1234ze

HFO-1234yf
Reference

- **Tube Contents:**
  - PAG lubricant
  - Copper, steel, aluminum
  - HFO-1234yf with 0.1% HFO-1234ze
- **Exposure is at 175°C for 2 weeks**
- **Test done in triplicate**
  - Pictures top left
  - HFO-1234yf (reference) with no 1234ze done earlier with the same exposure- bottom left
- **Results for the 3 samples**

| Sample | TAN |
|---|---|
| Pure 1234yf | 0.86 |
| 1000 ppm 1234ze in 1234yf | 1.14 |

- Initial MW of oil 1857
- Final MW of oil 1823
- Initial 1234ze Concentration 1000 ppm
- Final 1234ze concentration 919 ppm
  - •Difference can be accounted for by differential solubility of 1234ze in oil

***Conclusion: As an impurity, No Effect of HFO-1234ze at 1000 ppm level***

# HFO-1234yf – PAG lubricant General Conclusions

- **Air**
  - **Increases the TAN and fluoride during accelerated testing**
  - **Air needs to be controlled in MAC systems or supplemental additives will be needed for service and DIYer kits**

- **Water**
  - **Decreases the TAN and fluoride during accelerated testing**
  - **Water still needs to be controlled in MAC systems**

**Improved lubricant additive packages are being developed to meet even the tightest of requirements**

**We could use improved PAGs for hybrid systems**

# Honeywell Compressor Run Chemical Analysis

| Stability run 250g PAG 3 Oil, Test 1234yf PAG in clutchless externally controlled compressor | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| *Note: oil samples ~5g* | | | | | | | | | | | |
| **Sampling Interval Schedule** | | | | | | | | | | | |
| Hours | | Initial | 0 | 24 | 92 | 144 | 192 | 288 | 360 | 415 | post |
| Refrigerant | | | | x | x | | x | x | x | x | |
| Oil | | | x | x | x | x | x | x | x | x | x |
| **Test Rig Oil Analysis** | | | | | | | | | | | |
| Tests | units | | | | | | | | | | |
| ICP(M+,Total) µg/g | Fe | | <3 | 4.2 | 4.5 | <3 | 4.1 | <3 | 16.1 | 16.4 | 5.1 |
| | Cu | | 0.7 | 1.6 | 0.7 | 0.9 | 0.7 | 0.9 | 0.7 | <0.6 | 0.65 |
| | Al | | <5 | 10.7 | 5.4 | <5 | <5 | <5 | 6.9 | <5 | <5 |
| IC (µg/g) | Fluoride | 2.1 | 0.6 | 2.2 | 2.2 | 1.1 | 0.6 | 1.4 | 4.1 | 4 | 3.3 |
| | | | | | | | | | | | |
| Acid | mg KOH /g | <0.1 | 0.18 | <0.1 | <0.1 | <0.1 | <0.1 | 0.13 | <.1 | <.1 | <.1 |
| Water | ug/g | | 1616 | 2419 | 1161 | 960 | 1339 | 1112 | 1182 | 1141 | 542 |
| **Test Rig Vapor GC Analysis** | | | | | | | | | | | |
| Chemical Analysis | | | | | | | | | | | |
| Saturated HFC Impurity 1 | | 0.02% | | 0.02% | 0.02% | | 0.02% | 0.02% | 0.02% | 0.02% | |
| R-1234yf | | 99.80% | | 99.83% | 99.83% | | 99.85% | 99.83% | 99.84% | 99.83% | |
| R-1225ye | | 0.15% | | 0.13% | 0.12% | | 0.10% | 0.12% | 0.11% | 0.12% | |
| All Other Impurities | | 0.03% | | 0.03% | 0.03% | | 0.04% | 0.03% | 0.03% | 0.03% | |

**No Significant Change in System Breakdown Products Observed**

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# OEM Vehicle Validation Results – High Mileage

| COMPONENT | 1234yf<br>Apr-08<br>Lot BX043 | Vehicle 1<br>158,000 km<br>10 months | Vehicle 2<br>160,000 km<br>10 months | Vehicle 3<br>160,000 km<br>10 months |
|---|---|---|---|---|
| | | | | |
| R-1234yf, % | 99.97 | 99.5 | 99.4917 | 99.5415 |
| R-134a* (system contaminant), % | ND | 0.4433 | 0.4335 | 0.4209 |
| Sum R-1234yf + R-134a* | 99.97 | 99.9433 | 99.9252 | 99.9624 |
| R-1225yeZ, ppm | 98 | 173 | 130 | 105 |
| Other Refrig. Impurities, ppm | 194 | 296 | 398 | 222 |
| | | | | |
| Unknowns by FID, ppm<br>high MW containments (oil) | 0 | 124 | 220 | 56 |

R-134a* = Original R134a charge and impurities

# Storage Stability of HFO-1234yf

- 2 year test with refrigerant stored in warehouse
- Refrigerant before and after are identical
- NO refrigerant degradation

| COMPONENT | Lot#BX043 4/15/2008 | Lot#BX043 4/2/2010 |
|---|---|---|
| | | |
| | | |
| | | |
| FC-1234yf | 99.96 | 99.95 |
| FC-1225yeZ | 0.0100 | 0.0106 |
| Acetone/G-11 | 0.0065 | 0.0067 |
| FC-134a | ND | 0.0003 |
| Other Impurities | 0.0235 | 0.0324 |
| | | |

Pilot plant material contamination due to other operations, now corrected – only affected 1 batch in 2008

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# HFO-1234yf Purity for SAE J2844 (proposed)

- Honeywell recommends maintaining the generic 40 ppm limit for cumulative fluorinated unsaturated alkene impurities which have assigned OELs less than 1 ppm or an unassiged OELs.

- Higher concentration levels above 40 ppm of fluorinated unsaturated alkene impurities in refrigerants may be allowed provided:
  - sufficient toxicity data is available on the impurity to allow higher levels without threat to health and safety
  - higher concentration levels do not adversely affect refrigerant stability, reactivity in use, or polymerization potential.

- Honeywell recommends setting a limit by exception for HFO-1225yeZ of 150 ppm from known toxicity and stability/reactivity of this impurity at these levels.

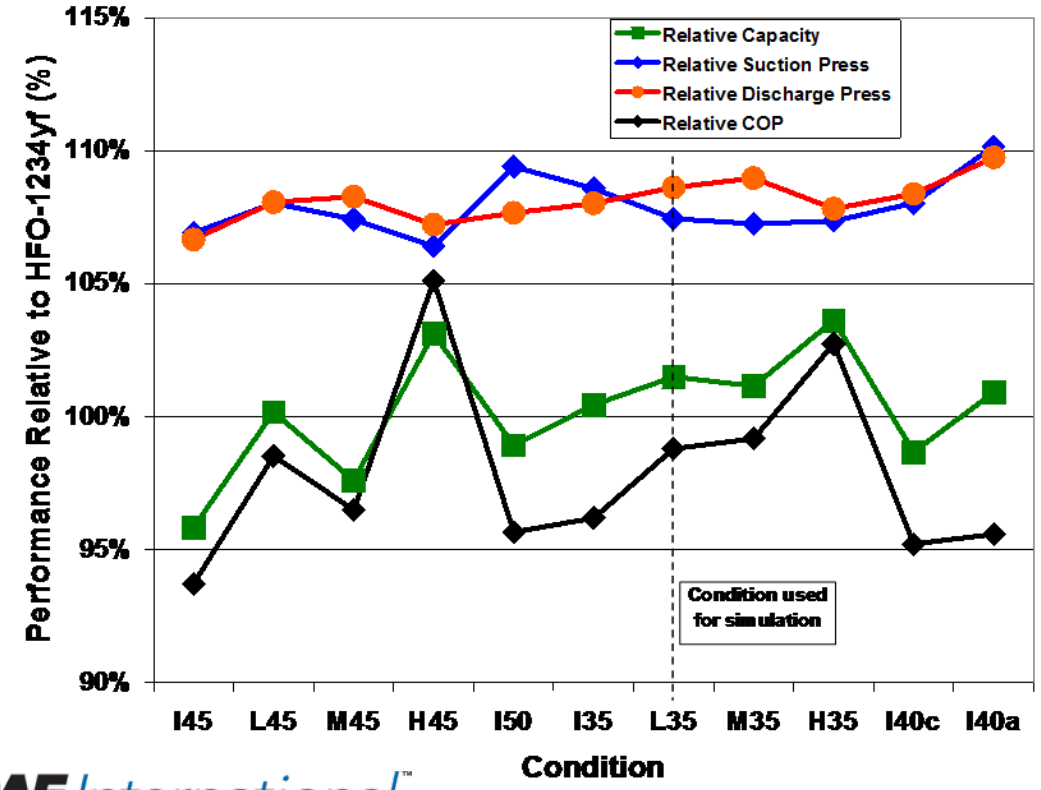
# HFO-1234yf Purity for SAE J2844 (proposed)

- **Manufactured HFO-1234yf shall meet SAE J2844:**

| | |
|---|---|
| HFO-1234yf | Min. 99.5% (w/w) |
| Moisture | Max. 25 ppm (w/w) |
| Non-Condensables | Max. 1.5% (v/v) in vapor at 23.9 ˚C |
| High Boiling Residue | Max. 100 ppm (v/v) |
| Impurity: HFO-1225yeZ | Max. 150 ppm (w/w) |
| Impurity: Total unspecified unsaturated compounds | Max. 40 ppm (w/w) |
| Impurity: Total organic compounds | Max. 5,000 ppm (w/w) |

# HFC-134a / HFO-1234yf Mix Test Results

- System bench tests were performed on a Opel Astra A/C system at Honeywell's Refrigerant Application Laboratory in 2008.
  - A 50/50 wt% mixture was compared against the pure refrigerants.
  - No changes made to the system.
  - Tests were run at the SAE CRP 45ºC and 35ºC.




- Modest increases in operating pressures
- Slight changes in performance
- Overall passenger comfort will not be compromised.

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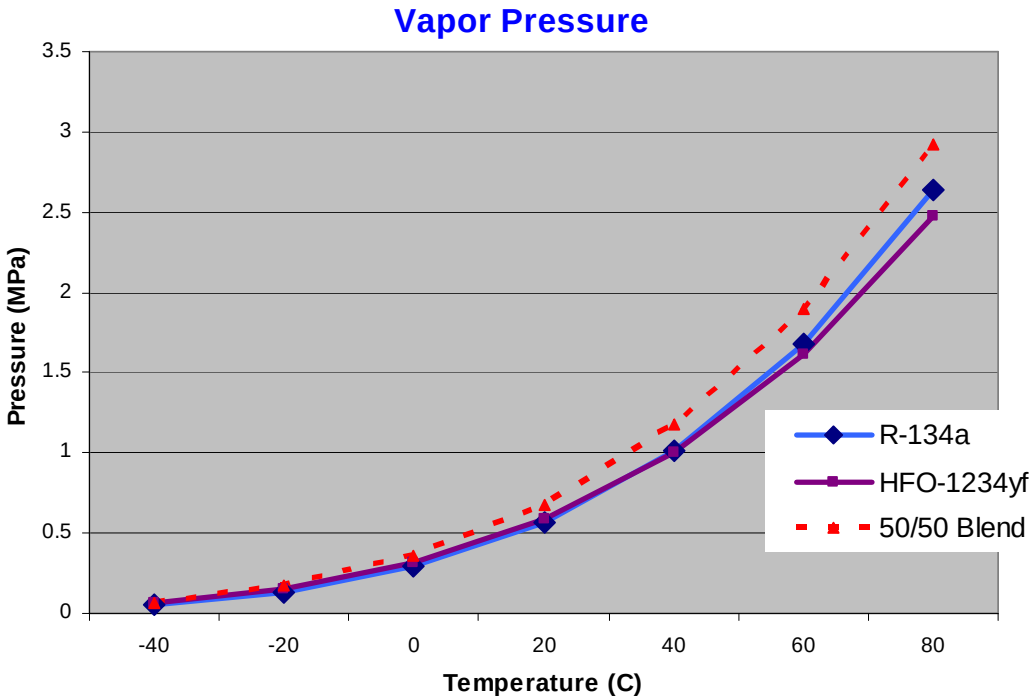
# Impact of Accidental Mixing




**What will happen if HFO-1234yf is accidentally mixed with HFC-134a?**

- **Minimal pressure effect, but will alter P-T relationship for servicing**
- **Potential impact on R/R/R segments (ease of separation, ARI 700 purity specs)**
- **Need proper service training, unique service fittings for HFO-1234yf vehicles**

***Regulations and training are needed to prevent mixing of HFC-134a and HFO-1234yf during servicing***

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# Dealing with R-134a Contamination of HFO-1234yf Systems – R\R\R equipment

- **Contamination of HFO-1234yf by R-134a can be misinterpreted as AIR by automated equipment**
- **Amount of air dissolved in liq. refrigerant can be estimated as:**

$$K_{air}(T) = K_{air@298K} * \exp\left(\frac{\Delta H}{R_{gas}}\left(\frac{1}{T} - \frac{1}{298K}\right)\right)$$

**where**

$$K_{air@298K} = 0.00173\frac{1}{\text{bar}} \quad \text{or} \quad 0.000119\frac{1}{\text{psi}}$$

$$R_{gas} = 8.314472\frac{\text{J}}{\text{mol*K}}$$

$$\Delta H = 16481\frac{\text{J}}{\text{mol}}$$

- **Solving for liquid and vapor mole fractions:**

$$x_{air} = \frac{P_{total} - P_{refr,sat}(T)}{\frac{1}{K_{air}(T)} - P_{refr,sat}(T)}$$

$$y_{air} = 1 - \frac{(1 - x_{air})P_{refr,sat}(T)}{P_{total}}$$

- **And then back to volume fractions in the vapor for engineers…**

$$Vol\%_{air} = y_{air} * \frac{Z_{1234yf}}{Z_{air}} = y_{air} * Z_{1234yf}$$

$$Z_{1234yf} \sim 0.975$$

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# Dealing with R-134a Contamination of HFO-1234yf Systems – R\R\R equipment

- **Standards require less than 1.5 vol% of air in refrigerant for purity specs.**

| Cylinder | Pressure Rise above Saturation Pressure (bar) | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Temperature | 0 | 0.03 | 0.04 | 0.05 | 0.06 | 0.07 | 0.08 | 0.09 | 0.1 | 0.2 | 0.3 |
| °C | Volume Fraction of Air in Refrigerant (vol%) | | | | | | | | | | |
| 0 | 0.00 | 0.92 | 1.22 | 1.53 | 1.83 | 2.12 | 2.42 | 2.71 | 3.01 | 5.83 | 8.50 |
| 10 | 0.00 | 0.67 | 0.89 | 1.11 | 1.33 | 1.55 | 1.77 | 1.98 | 2.20 | 4.30 | 6.31 |
| 20 | 0.00 | 0.50 | 0.66 | 0.83 | 0.99 | 1.16 | 1.32 | 1.48 | 1.64 | 3.23 | 4.77 |
| 30 | 0.00 | 0.38 | 0.50 | 0.63 | 0.75 | 0.88 | 1.00 | 1.13 | 1.25 | 2.47 | 3.66 |
| 40 | 0.00 | 0.29 | 0.39 | 0.49 | 0.58 | 0.68 | 0.78 | 0.87 | 0.97 | 1.92 | 2.85 |

| Cylinder | Pressure Rise above Saturation Pressure (psi) | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Temperature | 0.0 | 0.4 | 0.6 | 0.7 | 0.9 | 1.0 | 1.2 | 1.3 | 1.5 | 2.9 | 4.4 |
| °F | Volume Fraction of Air in Refrigerant (vol%) | | | | | | | | | | |
| 32 | 0.00 | 0.92 | 1.22 | 1.53 | 1.83 | 2.12 | 2.42 | 2.71 | 3.01 | 5.83 | 8.50 |
| 50 | 0.00 | 0.67 | 0.89 | 1.11 | 1.33 | 1.55 | 1.77 | 1.98 | 2.20 | 4.30 | 6.31 |
| 68 | 0.00 | 0.50 | 0.66 | 0.83 | 0.99 | 1.16 | 1.32 | 1.48 | 1.64 | 3.23 | 4.77 |
| 86 | 0.00 | 0.38 | 0.50 | 0.63 | 0.75 | 0.88 | 1.00 | 1.13 | 1.25 | 2.47 | 3.66 |
| 104 | 0.00 | 0.29 | 0.39 | 0.49 | 0.58 | 0.68 | 0.78 | 0.87 | 0.97 | 1.92 | 2.85 |

- **From PT relations, 5% R134a contamination of HFO-1234yf is sufficient to trip an air purge required to maintain the purity spec.**
  - Opposite is true for R134a with HFO-1234yf contamination

***Requires more than 5% contamination to be an air purge issue***

***Drawing liquid from a recovery cylinder and expanding through the manifold corrects air purge issue for air in MAC systems***

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# Recent Events

- **Honeywell and DuPont have announced a Joint Venture to Manufacture HFO-1234yf**
- **World-class source of supply to meet the growing demand faster than would be possible through either company's individual efforts**
- **The joint venture will begin supplying the refrigerant in the fourth quarter of 2011, in time to meet the European Union regulatory requirement for new type vehicles**
- **A world-scale plant will follow as demand grows.**

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