HFO-1234yf
Technology Update-Part I

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DuPont Fluoroproducts

February 11-12, 2009
Industry Update

• Auto OEMs continue strong support of HFO-1234yf as the leading MAC alternative

• Major milestones have been achieved through cooperative industry effort and open sharing of results
  • Toxicity/Environmental testing (DP-HW)
  • Risk assessments for flammability and health (SAE CRP-1234, JAMA, European Alliance)
  • System performance/LCCP evaluations (OEMs, SAE CRP-1234)
  • Materials compatibility/durability testing (SAE CRP-1234-2, JAMA, OEMs, Tier 1s and 2s)
  • Registration (REACH, SNAP, ASHRAE, etc)
# HFO-1234yf Toxicity Results

<table>
<thead>
<tr>
<th>Test</th>
<th>HFO-1234yf</th>
<th>HFC-134a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acute Lethality</td>
<td>No deaths 400,000 ppm</td>
<td>No deaths 359,700 ppm</td>
</tr>
<tr>
<td>Cardiac sensitization</td>
<td>NOEL &gt; 120,000 ppm</td>
<td>NOEL 50,000 ppm</td>
</tr>
<tr>
<td>13 week inhalation</td>
<td>NOAEL 50,000 ppm</td>
<td>NOAEL 50,000 ppm</td>
</tr>
<tr>
<td>Developmental (Rat)</td>
<td>NOAEL 50,000 ppm</td>
<td>NOAEL 50,000 ppm</td>
</tr>
<tr>
<td>Genetic Toxicity</td>
<td>Not Mutagenic</td>
<td>Not Mutagenic</td>
</tr>
<tr>
<td>13 week genomic (carcinogenicity)</td>
<td>Not active (50,000 ppm)</td>
<td>Not tested</td>
</tr>
<tr>
<td>2-yr carcinogenicity</td>
<td>Not required</td>
<td>Not carcinogenic</td>
</tr>
<tr>
<td>Environmental Tox</td>
<td>NOEL &gt; 83 mg/L (Pass)</td>
<td>NOEL &gt; 100 mg/L (Pass)</td>
</tr>
<tr>
<td>Developmental (Rabbit)</td>
<td>NOAEL 4,000 PPM,</td>
<td>NOAEL 2,500 PPM</td>
</tr>
<tr>
<td></td>
<td>LOAEL 5,500 PPM</td>
<td>LOAEL 10,000</td>
</tr>
<tr>
<td>1-Gen segment of 2-Gen Reproductive</td>
<td>Interim NOAEL 5,000 -15,000 ppm (6-hours exposures)</td>
<td>NOAEL 50,000 ppm (1-hour exposures)</td>
</tr>
</tbody>
</table>

**HFO-1234yf Has Low Toxicity**

- The HFO 1234yf WEEL was adopted at 500 ppm (8-hr TWA) by the AIHA WEEL Committee. AIHA Standards expects this assignment to be published in the 2009 set of WEELs. (AIHA -Independent group of toxicologist)
DuPont and Honeywell feel **comfortable** with all toxicity test results conducted to date and will **continue the commercialization** of HFO-1234yf for use in **MAC**

Based on toxicity testing conducted to date, we believe HFO-1234yf will not be classified as a developmental or reproductive toxin, and it will likely be classified as ASHRAE Class A (low toxicity).

There **appear to be no health safety hazards or properties that would preclude the safe use of HFO-1234yf in MAC applications.**
REACH

• 2,3,3,3-tetrafluoroprop-1-ene (Cas 754-12-1)
  • Registered under REACH Directive 67/548/EEC (Elnics), VII-A status
    - EC #: 468-710-7
    - Threshold 10 MT p.a. (50 MT cumulative)
    - Honeywell REACH Registration #: 01-0000019665-61-000
    - Notification is company specific
      • DuPont has been granted access to Honeywell notification

• Update required once next tonnage threshold reached (inform only)
• 1000+ T Update registration file is complete - submit February 2009
• ECHA has three weeks to conduct completeness check of each registration

HFO-1234yf Registered Under REACH; Data Threshold is 10 MT p.a.
US Regulatory -SNAP

• US SNAP ruling prohibited use of flammables in MACS (June, 1995)
• US SNAP issued a Final Rule on HFC-152a (June, 2008) to allow its conditional use in mobile air conditioning
• US SNAP has not issued a Final Rule on CO2 to allow its use in mobile air conditioning

• US EPA Industry Update
  • EPA- No significant barriers regarding use flammable refrigerants in Europe, Japan, or other countries (e.g., Australia, Canada).
  • Four states flammable refrigerants banned in MAC applications.
  • Alliance of Automobile Manufacturers is working with support of EPA to remove those barriers for SNAP listed refrigerants

• Most regulations will primarily impact
  • Transportation/storage of flammables at manufacturing sites and service shops.
  • Rules are often managed at state and local levels.
US SNAP Overview

• HFO-1234yf SNAP application submitted to EPA in 2007
• Official “completeness letter” received from EPA July 8, 2008
• 90 Day clock for EPA to comment on our submission ended October 8, 2008

• If EPA has no significant issues, next steps are:
  • Draft a "Proposed Rule of Law" statement which includes HFO-1234yf and identify any conditions of use (currently waiting for PMN office)
  • Have the US Office of Management and Budget (OMB) review and approve the Proposed Rule
  • Publish the Proposed Rule in the Federal Register
  • Have a public comment period for interested parties to make comments
  • Complete final EPA SNAP approval through publication of a Final Rule
  • This process takes about a year due to various US government agencies involved
# US Codes and Standards As Applied to HFO-1234yf

<table>
<thead>
<tr>
<th></th>
<th>Propane</th>
<th>HFC-152a</th>
<th>HFC-32</th>
<th>NH3</th>
<th>HFC-134a</th>
<th>HFO-1234yf</th>
<th>Gasoline**</th>
<th>Hydrogen**</th>
<th>Ethanol**</th>
</tr>
</thead>
<tbody>
<tr>
<td>LFL (vol% in Air)</td>
<td>2.2</td>
<td>3.9</td>
<td>14.4</td>
<td>15</td>
<td>N/A</td>
<td>6.2</td>
<td>1.3</td>
<td>4</td>
<td>3.3</td>
</tr>
<tr>
<td>UFL (vol% in Air)</td>
<td>10</td>
<td>16.9</td>
<td>29.3</td>
<td>28</td>
<td>N/A</td>
<td>12.3</td>
<td>7.1</td>
<td>75</td>
<td>19.0</td>
</tr>
<tr>
<td>Minimum Ignition Energy (mJ)</td>
<td>0.25</td>
<td>0.38</td>
<td>30-100*</td>
<td>100-300*</td>
<td>N/A</td>
<td>&gt;5000</td>
<td>0.29</td>
<td>0.016</td>
<td>0.65</td>
</tr>
<tr>
<td>Autoignition Temperature (°C)</td>
<td>470</td>
<td>454</td>
<td>648</td>
<td>750</td>
<td>&gt;743</td>
<td>405</td>
<td>230-280</td>
<td>585</td>
<td>360</td>
</tr>
<tr>
<td>Heat of Combustion (kJ/g)</td>
<td>46.3</td>
<td>16.5</td>
<td>9.4</td>
<td>18.6</td>
<td>4.2</td>
<td>9.5</td>
<td>47</td>
<td>142.9</td>
<td>29.8</td>
</tr>
<tr>
<td>Burning Velocity (cm/s)</td>
<td>46</td>
<td>23</td>
<td>6.7</td>
<td>7.2</td>
<td>N/A</td>
<td>1.5</td>
<td>34</td>
<td>265-325</td>
<td>58</td>
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<tr>
<td>Flammability Index-Low value preferred</td>
<td>R</td>
<td>1.99</td>
<td>1.78</td>
<td>1.31</td>
<td>N/A</td>
<td>0.97</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>0.55</td>
<td>0.5</td>
<td>0.33</td>
<td>0.27</td>
<td>N/A</td>
<td>0.27</td>
<td>0.57</td>
<td>0.77</td>
</tr>
<tr>
<td></td>
<td>RF</td>
<td>56.7</td>
<td>16.6</td>
<td>4.6</td>
<td>N/A</td>
<td>3.6</td>
<td>62.8</td>
<td>41.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>RF2</td>
<td>37.2</td>
<td>17.9</td>
<td>2.3</td>
<td>N/A</td>
<td>0.06</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Savery, et. Al.
** Brandes and Ural

**Key Takeaways**
- HFO-1234yf flammability characteristics are “milder than” those of hydrocarbon gases or HFC-152a
- US Codes, (NFPA 58, NPFA 59A, NFPA1) may be overly conservative with regard to HFO-1234yf.
- HFO-1234yf flammability properties similar to ammonia for electrical equipment classification.

**What’s Next?**
Work with NFPA, the refrigerants industry, and auto industry to properly incorporate HFO-1234yf for product use and application.
## HFO-1234yf SAE Standards in Preparation

<table>
<thead>
<tr>
<th>SAE Std #</th>
<th>Standard Title</th>
</tr>
</thead>
<tbody>
<tr>
<td>J2772</td>
<td>Refrigerant Passenger Compartment Concentrations Measurement under AC System Refrigerant Leakage Conditions</td>
</tr>
<tr>
<td>J2773</td>
<td>Refrigerant Guidelines for Safety and Risk Analysis for use in Mobile Air Conditioning Systems</td>
</tr>
<tr>
<td>J2842</td>
<td>HFO-1234yf and R744 Evaporator Design Certification for OEM and Service Replacement</td>
</tr>
<tr>
<td>J2843</td>
<td>HFO-1234yf Refrigerant Recovery/Recycle/Recharging Equipment for Mobile Air Conditioning Systems</td>
</tr>
<tr>
<td>J2844</td>
<td>HFO-1234yf Refrigerant Purity and Container Requirements for Refrigerant used in Mobile Air Conditioning Systems</td>
</tr>
<tr>
<td>J2845</td>
<td>Technician Certification for Servicing and Refrigerant Containment of A/C Systems</td>
</tr>
<tr>
<td>J2851</td>
<td>HFO-1234yf Refrigerant Recovery Only Equipment for Mobile Air Conditioning Systems</td>
</tr>
<tr>
<td>J2887</td>
<td>HFO-1234yf Service Standards for Mobile Air Conditioning Systems</td>
</tr>
<tr>
<td>J2888</td>
<td>HFO-1234yf Service Hose, Fittings and Couplers for Mobile Refrigerant Systems and Service Equipment</td>
</tr>
</tbody>
</table>

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**Auto industry providing HFO-1234yf guidance for product usage**
Service Readiness - Service Shops

Service Shops

- Refrigerant for service is supplied through distributors and aftermarket channels.
- Service technicians will need to have additional safety training on proper product handling/use guidelines.
- Modifications proposed for HFO-1234yf automotive air-conditioning service locations.

New 2009 US EPA Technician Certification

- To Comply: All new technicians must be certified by a provider currently listed by EPA.
- Technicians certified prior to Dec. 2008 are not required to re-certify.

Service industry preparing for HFO-1234yf

Reference – Ward Atkinson, MACS 2009
Service Readiness-Equipment

Recovery/Recycle/Recharging Equipment

- SPX Solutions (Robinair) has HFO-1234yf R/R/R machines in product development phase.

- Recovery machines rated for other flammable products (non-sparking controls) currently available within the EU.
  - Other EU companies that have flammable experience
    - Agramkow Denmark, http://www.agramkow.dk
    - WAECO Germany, http://www.airconservice.de

Reference-SPX Solutions
# HFO-1234yf Properties

<table>
<thead>
<tr>
<th>Properties</th>
<th>1234yf</th>
<th>134a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiling Point, $T_b$</td>
<td>-29°C</td>
<td>-26°C</td>
</tr>
<tr>
<td>Critical Point, $T_c$</td>
<td>95°C</td>
<td>102°C</td>
</tr>
<tr>
<td>$P_{vap}$, MPa (25°C)</td>
<td>0.677</td>
<td>0.665</td>
</tr>
<tr>
<td>$P_{vap}$, MPa (80°C)</td>
<td>2.44</td>
<td>2.63</td>
</tr>
<tr>
<td>GWP (100 ITH)</td>
<td>4</td>
<td>1410</td>
</tr>
<tr>
<td>ODP</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

**Vapor Pressure**

![Graph showing vapor pressure comparison between 134a and HFO-1234yf](#)

*Vapor Pressure similar to HFC-134a*
HFO-1234yf PH Diagram
R-134a vs. HFO-1234yf

Pressure - Enthalpy

Red – HFO-1234yf
Blue – R-134a

HFO-1234yf Experimental Data Relative to R-134a

- COP = 101%
- Capacity = 100%
- Vol. Disp = 100%
- Massflow = 120%
- Charge = 95%

Reference State:
- h = 200 kJ/kg, s = 1.00 kJ/kg-K
- sat. liq at 0 ºC

R134a-5/8” suction, HFO-1234yf-3/4” suction
Improved Fuel Consumption with IHX

**Internal Heat Exchanger Component**

**Value to Customer**
- A 10-20% reduction in the amount of fuel used to power the a/c system
- Cost effective solution to recover A/C performance loss due to new R1234yf refrigerant

**Delphi Advantage**
- Higher Performance / Easier to Package than competitive designs
  - Suction side passage has 50% less pressure drop
  - Length is 30% less

**Functionality**
- Enables the same cooling performance with less compressor power – captures waste energy

**Availability**
- 2011 MY

HFO-1234yf IHX development will continue to provide LCCP benefits
Product Performance

SAE CRP-1234 Data GREEN MAC LCCP
LCCP CO₂-Equivalent Emissions per Year

Based on GREEN-MAC-LCCP Version 2

Reference-Hill, VDA Wintermeeting 2008
HFO-1234yf Summary

Major milestones have been achieved through cooperative industry effort and open sharing of results

- Toxicity/Environmental testing (DP-HW)
- Risk assessments for flammability and health (SAE CRP-1234, JAMA, European Alliance)
  - Several risk assessments completed, with similar conclusions
- System performance/LCCP evaluations (OEMs, SAE CRP-1234)
  - Various LCCP evaluations done showing LCCP benefit of HFO-1234yf compared to HFC-134a
- Materials compatibility/durability testing (SAE CRP-1234-2, JAMA, OEMs, Tier 1s and 2s)
  - Current materials of construction are compatible with HFO-1234yf
- Registration (REACH, SNAP, ASHRAE, etc)
  - Appropriate regulatory items have been submitted and are in process
HFO-1234yf Overall Summary

- **Excellent environmental properties**
  - Very low GWP of 4, Zero ODP, lowest LCCP
  - Atmospheric chemistry determined and published
- **Low toxicity**
  - Low acute and chronic toxicity
  - Significant testing completed
- **System performance very similar to R-134a**
  - Excellent COP and Capacity, 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
- **Global Solution**
  - Good performance in all climates
  - Compatibility with current technology allows for rapid global adoption
Additional Information

For further information on HFO-1234yf please visit:

www.SmartAutoAc.com
www.refrigerants.dupont.com
www.genetron.com
www.1234facts.com
Thank You!