Recent Developments of Zero ODP, Low GWP Clean Fire Suppression Agents

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What is a Clean Agent?


- 3.3.6 Clean Agent. Electrically nonconducting, volatile, or gaseous fire extinguishing agent that does not leave a residue upon evaporation

No residue
No cleanup
No downtime
Halon Era: 1960s to 1994:

- Halon 1301 – total flooding
- Halon 1211 – streaming applications
  - No corrosive or abrasive residues
    No damage to sensitive/expensive asset
  - No cleanup required after discharge
    No business interruption

Protection of expensive, sensitive, mission-critical assets
Cost of Business Interruption

Cost of datacenter downtime is high and getting higher

Average cost per minute increased 41% from 2010

2010: $5,617 per minute

2013: $7,908 per minute

Source: Ponemon Institute 2013
The Halon Era: 1960s to 1994

Halon 1301/Halon 1211 Applications

- Electronics facilities
- Computer rooms
- Communications equipment rooms
- Oil & gas industry
  - pipeline pumping stations
  - offshore platforms
- Shipboard machinery spaces
- Museums
- Libraries
The Halons were near ideal…
– What Happened?
Ozone Depletion

1. CFCs released
2. CFCs rise into ozone layer
3. UV releases Cl from CFCs
4. Cl destroys ozone
5. Depleted ozone -> more UV
6. More UV -> more skin cancer

Source: U.S. EPA
Mid 1980s Thinkers: “Halon is to be Phased Out - Now What?”
The Search for “Son of Halon” ➢ mid-1980s to Present
The Halon Era: 1960s to 1994

What made the Halons “Ideal Fire Extinguishing Agents” ?

- Clean
- Efficient fire suppression
- Chemically inert
  - Storage stable
  - Non-reactive chemically
- Electrically non-conducting
- Low Toxicity
- Low Cost

A unique combination of properties
Properties of the Ideal Halon Replacement

• Clean
• Efficient fire suppression
• Chemically inert
  ➢ Long term storage stability
  ➢ No chemical reactions with water, fuels, assets
• Electrically non-conducting
• Low toxicity
• Zero ODP
• Zero GWP
• Reasonable manufacturing cost

No replacement has been found which satisfies ALL of the above requirements
100s of Researchers....
1000s of Compounds Screened Later........

Halon Replacements
- Commercialized Agents
Comparison of Halon 1301 Replacements

X = provides desired property

<table>
<thead>
<tr>
<th>Ideal Halon 1301 Replacement</th>
<th>Halon 1301</th>
<th>HFCs</th>
<th>Inert Gases</th>
<th>Perfluoroketones</th>
</tr>
</thead>
<tbody>
<tr>
<td>High weight efficiency</td>
<td>XX</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gas at ambient temperature</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Low chemical reactivity</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electrically nonconducting</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Low toxicity</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lack of metabolism</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Low agent cost</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Low system cost</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Low number agent cylinders</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Low storage volume</td>
<td>X</td>
<td>X</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>Low system footprint</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Low cylinder pressure rating</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Low manifold pressure rating</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Low negative pressures during discharge</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Low positive pressures during discharge</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Slow stratification</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zero ODP (ozone depletion potential)</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zero GWP (global warming potential)</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>VOC exempt (no contribution to smog)</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**HFCs offer the best overall combination of the properties desirable in a Halon replacement**
Global Warming: Impact of HFCs in Fire Extinguishing Applications

High GWP value ≠ High impact on global warming
Low GWP values ≠ Low impact of global warming

Impact = GWP x Emissions

Impact on Global Warming

<table>
<thead>
<tr>
<th>Gas</th>
<th>Impact on Global Warming, Tg CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>5,613</td>
</tr>
<tr>
<td>HFCs in Fire Applications</td>
<td>0.9</td>
</tr>
</tbody>
</table>

CO₂, GWP = 1
FM-200®, GWP = 3500

Source: US EPA (2013)

Based on US EPA 2013
Clean Agent Program

Goal: Discover and commercialize a range of new clean fire extinguishing agents to extend our current portfolio and satisfy the safety, environmental and performance requirements of clean agent users around the world.
Total Flooding Agents

• High mass efficiency
• Chemically inert
  • *No reaction with water, common solvents*
  • *Long term storage stability*
• High volatility
  • *bp -70 to + 40 °C*
• Electrically non-conducting
• Low toxicity
• Cost effective
Total Flooding Agents
Fire Suppression Testing

- Class A (solid) Fuels
  - UL 2166 Full-scale Tests
    - Plastic Sheets (PMMA, ABS, PP)
    - Wood crib
    - 100 m³ enclosure; 50 kg per single test run

95% of clean agent applications are Class A/Class C hazard protection
Class A Performance

Lab Scale Method Developed

DuPont-developed rod tests

- Modification of cup burner apparatus
- Plastic rod – special design
- Laboratory scale: 300 g requirement
- Excellent agreement with UL 2166 results

FM-200®, FE-25™, Novec™ 1230
Total Flooding Agents
Fire Suppression Testing

• Class B (liquid, gaseous) Fuels
  Cup burner apparatus
  • Standardized apparatus (NFPA 2001/ISO 14520)
Small Scale Total Flooding Tests

- 0.6 m$^3$ Lexan test enclosure
- Class B “pan” fire tests
- Class A tests

*plastic pieces (PMMA, PP, ABS)*

“mini wood crib”
# Physical & Chemical Properties of Total Flooding Agents for Occupied Areas

<table>
<thead>
<tr>
<th>Property</th>
<th>Halon 1301</th>
<th>FM-200®</th>
<th>Novec™ 1230</th>
<th>Flooding Candidate 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Formula</td>
<td>CF₃Br</td>
<td>CF₃CHFCF₃</td>
<td>CF₃CF₂CF(CO)-CF(CF₃)₂</td>
<td>Proprietary</td>
</tr>
<tr>
<td>Boiling point (°C)</td>
<td>-58</td>
<td>-17</td>
<td>49</td>
<td>31</td>
</tr>
<tr>
<td>Liquid density (g/cm³ @ 25 °C)</td>
<td>1.54</td>
<td>1.38</td>
<td>1.72</td>
<td>1.3</td>
</tr>
<tr>
<td>Chemical Reactivity</td>
<td>Low</td>
<td>Low</td>
<td>High</td>
<td>Low</td>
</tr>
</tbody>
</table>
Toxicological Properties of Total Flooding Agents for Occupied Areas

<table>
<thead>
<tr>
<th>Property</th>
<th>Halon 1301</th>
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<th>Flooding Candidate 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>4h LC$_{50}$, ppm</td>
<td>&gt;800,000</td>
<td>&gt;800,000</td>
<td>&gt;100,000</td>
<td>&gt;231,000</td>
</tr>
<tr>
<td>CS NOAEL, % v/v</td>
<td>5.0</td>
<td>9.0</td>
<td>10.0</td>
<td>10.0</td>
</tr>
<tr>
<td>CS LOAEL, % v/v</td>
<td>7.5</td>
<td>10.5</td>
<td>&gt; 10.0</td>
<td>12.5</td>
</tr>
</tbody>
</table>
Fire Suppression Properties of Total Flooding Agents for Occupied Areas

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<tr>
<th>Property</th>
<th>Halon 1301</th>
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<th>Novec\textsuperscript{TM} 1230</th>
<th>Flooding Candidate 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Class A MDC, % v/v</td>
<td>5.0</td>
<td>6.7</td>
<td>4.5</td>
<td>5.6</td>
</tr>
<tr>
<td>Class B MDC, % v/v  \textsuperscript{a}</td>
<td>5.0</td>
<td>8.7</td>
<td>5.9</td>
<td>6.9</td>
</tr>
<tr>
<td>Class C MDC, % v/v</td>
<td>5.0</td>
<td>7.0</td>
<td>4.7</td>
<td>6.3</td>
</tr>
<tr>
<td>Relative mass efficiency, heptane hazard</td>
<td>0.48</td>
<td>1.00</td>
<td>1.26</td>
<td>1.00</td>
</tr>
<tr>
<td>Relative mass efficiency, Class C Hazard</td>
<td>0.60</td>
<td>1.00</td>
<td>1.25</td>
<td>1.00</td>
</tr>
</tbody>
</table>

\textbf{Mass Efficiency:}

Halon 1301 > Flooding Candidate 1 ~ HFC-227ea > FK-5-1-12

Higher mass required
Flooding Candidate 1: Determination of GWP

Experimental Data
- Infrared Absorption Spectrum
- Rate Constant for reaction with OH radical
  - Reaction with OH is primary atmospheric sink
  - Laser Photolysis – Laser Induced Fluorescence Technique

Results

\[ k(272 \, K) = 3.2 \times 10^{-13} \, \text{cm}^3 \, \text{molecule}^{-1} \, \text{s}^{-1} \]

Lifetime = 36 days
GWP (100 year time horizon) = 2
Environmental Properties of Total Flooding Agents for Occupied Areas

<table>
<thead>
<tr>
<th>Property</th>
<th>Halon 1301</th>
<th>FM-200®</th>
<th>Novec™ 1230</th>
<th>Flooding Candidate 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>ODP</td>
<td>10</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Atmospheric Lifetime, years</td>
<td>65</td>
<td>34.2</td>
<td>0.02</td>
<td>0.10</td>
</tr>
<tr>
<td>GWP (100 y ITH)</td>
<td>7140</td>
<td>3220</td>
<td>1</td>
<td>2</td>
</tr>
</tbody>
</table>
Total Flooding Candidate 1

Suitable for the protection of normally occupied areas containing Class A, Class B, and Class C hazards

- $4h \text{LC}_{50} > 23.1\%$
- $\text{CS NOAEL} = 10\%$
- $\text{CS LOAEL} = 12.5\%$
- $\text{MDC Class A} = 5.6\%$
- $\text{MDC Class B} = 6.9\%$
- $\text{MDC Class C} = 6.3\%$

95% Clean Agent Applications
Total Flooding Candidate 1

- Current Activity
  - Process scale-up completed
  - Intermediate & Full-scale fire testing
Clean Agent Development

Streaming Agents

• High mass efficiency
• Chemically inert
  • *No reaction with water, common solvents*
  • *Long term storage stability*
• Liquid or high bp gas
  • *bp -10 to + 40 °C*
• Electrically non-conducting
• Toxicity
  • *Equal to or better than Halon 1211 or HCFC-123*
• Cost effective
# Physical & Chemical Properties of Streaming or Non-Occupied Area Agents

<table>
<thead>
<tr>
<th>Property</th>
<th>Halon 1211</th>
<th>2-BTP</th>
<th>Streaming/Non-occupied Area Candidate 1 (SC1)</th>
<th>Streaming/Non-occupied Area Candidate 2 (SC2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Formula</td>
<td>CF$_2$BrCl</td>
<td>CF$_3$CBr=CH$_2$</td>
<td>Proprietary</td>
<td>Proprietary</td>
</tr>
<tr>
<td>ODP</td>
<td>3</td>
<td>0.0028</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Atmospheric lifetime (y)</td>
<td>16</td>
<td>0.02</td>
<td>TBD</td>
<td>TBD</td>
</tr>
<tr>
<td>GWP (100 year ITH)</td>
<td>1890</td>
<td>0.26</td>
<td>&lt; 20 est.</td>
<td>&lt; 20 est.</td>
</tr>
<tr>
<td>Boiling point (°C)</td>
<td>-4</td>
<td>34</td>
<td>31</td>
<td>18</td>
</tr>
<tr>
<td>Liquid density (g/cm$^3$ @25 °C)</td>
<td>1.8</td>
<td>1.65</td>
<td>1.38</td>
<td>1.3</td>
</tr>
<tr>
<td>Chemical Reactivity</td>
<td>Low</td>
<td>Low</td>
<td>Low</td>
<td>Low</td>
</tr>
</tbody>
</table>
Toxicological Properties of Streaming or Non-Occupied Area Agents

<table>
<thead>
<tr>
<th>Property</th>
<th>Halon 1211</th>
<th>2-BTP</th>
<th>Streaming/Non-occupied Area Candidate 1 (SC1)</th>
<th>Streaming/Non-occupied Area Candidate 2 (SC2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4h LC$_{50}$, ppm</td>
<td>31,300</td>
<td>&gt; 20,000</td>
<td>&gt; 102,900</td>
<td>120,000</td>
</tr>
<tr>
<td>CS NOAEL, % v/v</td>
<td>0.5</td>
<td>0.5</td>
<td>1.25</td>
<td>2.50</td>
</tr>
<tr>
<td>CS LOAEL, % v/v</td>
<td>1.0</td>
<td>1.0</td>
<td>2.50</td>
<td>&gt; 2.50</td>
</tr>
</tbody>
</table>

Candidate 2 exhibits toxicity profile superior to that of Halon 1211 and 2-BTP
# Fire Suppression Properties of Streaming or Non-Occupied Area Agents

<table>
<thead>
<tr>
<th>Property</th>
<th>Halon 1211</th>
<th>2-BTP</th>
<th>Streaming/Non-occupied Area Candidate 1 (SC1)</th>
<th>Streaming/Non-occupied Area Candidate 2 (SC2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Class A MDC, % v/v</td>
<td>5.0</td>
<td>?</td>
<td>5.6</td>
<td>4.8</td>
</tr>
<tr>
<td>Class B MDC, % v/v</td>
<td>5.0</td>
<td>6.1</td>
<td>7.3</td>
<td>6.2</td>
</tr>
<tr>
<td>Class C MDC, % v/v</td>
<td>5.0</td>
<td>?</td>
<td>6.3</td>
<td>5.0</td>
</tr>
<tr>
<td>Relative mass efficiency, heptane</td>
<td>1.0</td>
<td>1.3</td>
<td>2.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Relative mass efficiency, Class A</td>
<td>1.3</td>
<td>?</td>
<td>1.9</td>
<td>1.0</td>
</tr>
</tbody>
</table>

*Candidate 2 exhibits a mass efficiency equal to or superior to that of Halon 1211 and a mass efficiency superior to that of 2-BTP*
Summary

- **Total flooding: Occupied Areas**
  
  *Development of a promising total flooding candidate suitable for use in normally occupied areas based on toxicological testing and small-scale fire testing*

  - Suitable for use in normally occupied areas
    - Class A, Class B, Class C hazards
  - Zero ODP
  - Low GWP
  - Good mass efficiency
  - Low chemical reactivity

  *Further evaluation in progress*
Summary

• **Streaming or Non-occupied Areas**
  
  *Development of several promising candidates based on toxicological testing and small-scale fire testing*

  • Candidate #2 meets or exceeds Halon 1211 in mass efficiency and has superior toxicity profile
  • Candidate #2 exceeds 2-BTP in mass efficiency and has superior toxicity profile
  • Zero ODP
  • Low GWP
  • Low chemical reactivity

*Further evaluation in progress*