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 $\rightarrow$ more UV
6 - More UV $\rightarrow$ 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>X</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>X</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>X</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>X</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>X</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>X</td>
<td></td>
</tr>
<tr>
<td>Zero GWP (global warming potential)</td>
<td></td>
<td></td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>VOC exempt (no contribution to smog)</td>
<td>X</td>
<td>X</td>
<td>X</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

- **CO₂**: 85%
- All other GHGs: 99.99%
- HFCs in Fire Applications (0.01%)

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 m³ 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>
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</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>
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## Fire Suppression Properties of Total Flooding Agents for Occupied Areas

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</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 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>

**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**

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

Lifetime = 36 days

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

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<thead>
<tr>
<th>Property</th>
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<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

- $4h \text{LC}_{50} > 23.1\%$
- $\text{CS NOAEL} = 10\%$
- $\text{CS LOAEL} = 12.5\%$
- $\text{MDC Class A} = 5.6\%$
- $\text{MDC Class B} = 6.9\%$
- $\text{MDC Class C} = 6.3\%$
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&lt;sub&gt;2&lt;/sub&gt;BrCl</td>
<td>CF&lt;sub&gt;3&lt;/sub&gt;CBr=CH&lt;sub&gt;2&lt;/sub&gt;</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&lt;sup&gt;3&lt;/sup&gt; @ 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>
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</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 to 100,000</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*