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
The Halon Era: 1960s to 1994

Halon 1301: CF$_3$Br
- Total flooding applications

Halon 1211: CF$_2$BrCl
- Portable, local applications

“Clean Agents”
- No corrosive or abrasive residues left following extinguishment

Water, foam, powder – secondary damage due to agent can exceed damage due to fire
Halon 1301/Halon 1211: “Clean Agents”

Clean Agents

- No corrosive or abrasive residues
  \textit{No damage to sensitive/expensive assets}

- No cleanup required after discharge
  \textit{No business interruption}

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

#### Business Sector

<table>
<thead>
<tr>
<th>Business Sector</th>
<th>Revenue Loss per Hour</th>
<th>Productivity Loss per Hour</th>
</tr>
</thead>
<tbody>
<tr>
<td>Financial</td>
<td>$9,997,500</td>
<td>$3640</td>
</tr>
<tr>
<td>Retail</td>
<td>$397,500</td>
<td>$2580</td>
</tr>
<tr>
<td>Healthcare</td>
<td>$157,500</td>
<td>$1250</td>
</tr>
<tr>
<td>Manufacturing</td>
<td>$59,930</td>
<td>$3,060</td>
</tr>
<tr>
<td>Public Sector</td>
<td>$0</td>
<td>$850</td>
</tr>
</tbody>
</table>

Ponemon Institute, 2010

#### Revenue Loss per hour

- **30%** respondents estimate > $50,000 revenue loss per hour

IDC Business Value Research, 2009-2011
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
Commercialized Halon 1301 Replacements

• Hydrofluorocarbons (HFCs)
  ➢ HFC-227ea:  FM-200® $CF_3CHFCF_3$
  ➢ HFC-125:   FE-25™ $CF_3CF_2H$
  ➢ HFC-23:   FE-13™ $CF_3H$

• Hydrochlorofluorocarbons (HCFCs)

  Subject to Phase-out

• Inert Gases
  ➢ IG-541:   Inergen™ $Ar/N_2/CO_2$
  ➢ IG-55:   Argonite™ $Ar/N_2$

• Perfluorinated Ketones
  ➢ FK-5-1-12:   Novec™ 1230 $CF_3CF_2C(O)CF(CF_3)_2$
Commercialized Halon 1211 Replacements

- **Hydrofluorocarbons (HFCs)**
  - HFC-236fa: FE-36™ CF₃CH₂CF₃

- **Hydrochlorofluorocarbons (HCFCs)**
  - Halotron® I: HCFC-123 + Ar + CF₄
## Comparison of Halon 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>
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<tr>
<td>Gas at ambient temperature</td>
<td>X</td>
<td>X</td>
<td>X</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>X</td>
<td></td>
</tr>
<tr>
<td>Lack of metabolism</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Low agent cost</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Low system cost</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Low number agent cylinders</td>
<td>X</td>
<td>X</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>Low storage volume</td>
<td>X</td>
<td>X</td>
<td></td>
<td></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>X</td>
<td></td>
</tr>
<tr>
<td>Low positive pressures during discharge</td>
<td>X</td>
<td>X</td>
<td></td>
<td>X</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>X</td>
<td></td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>VOC exempt (no contribution to smog)</td>
<td>X</td>
<td>X</td>
<td></td>
<td>X</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 FE Applications (0.01%)

Source: US EPA (2013)
Recent Developments in Clean Agents
Clean Agent Program
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
Toxicological Requirements = BIG Challenge

Tox Requirements driven by Clean Agent Standards

- MDC < 4h $LC_{50}$
- MDC < Cardiac LOAEL
- MDC < Cardiac NOAEL

$MDC = Minimum Design Concentration$
$LOAEL = Lowest observed adverse effect level$
$NOAEL = No observed adverse effect level$

Much higher bar compared to refrigeration, foam blowing, propellant, & solvent tox requirements
Toxicological Testing

No Qualitative Structure Activity Relationships (QSAR) available for 4h LC$_{50}$ or cardiac sensitization tests

Agent screening: 1h LC$_{50}$

- 200 - 300 g material = $$
- $10,0000

4 h LC$_{50}$ and Cardiac Sensitization Tests

- 50 – 60 kg material = $$$$$
- $150,000 for tox tests
Fire Suppression Testing

Class A

Plastic Rod Test
Total Flood Tests

Class B

Cup Burner Test
Total Flood Tests
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

HFC-227ea, HFC-125, FK-5-1-12
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>HFC-227ea</th>
<th>FK-5-1-12</th>
<th>Flooding Candidate 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Formula</td>
<td>CF$_3$Br</td>
<td>CF$_3$CHFCF$_3$</td>
<td>CF$_3$CF$_2$CF(CO)-CF(CF$_3$)$_2$</td>
<td>Proprietary</td>
</tr>
<tr>
<td>ODP</td>
<td>10</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Atmospheric lifetime (y)</td>
<td>65</td>
<td>34.2</td>
<td>0.02</td>
<td>TBD</td>
</tr>
<tr>
<td>GWP (100 year ITH)</td>
<td>7140</td>
<td>3660</td>
<td>1</td>
<td>&lt; 20 est.</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/cm$^3$ @ 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>
<th>HFC-227ea</th>
<th>FK-5-1-12</th>
<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

<table>
<thead>
<tr>
<th>Property</th>
<th>Halon 1301</th>
<th>HFC-227ea</th>
<th>FK-5-1-12</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 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>

\(^a\) heptane

**Mass Efficiency:**

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

Higher mass required
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 to produce 1000 kg*
  - *Intermediate & Full-scale fire testing*
  - *Additional material of construction testing*
  - *GWP determination in progress*
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
Portables Development

- Complex interaction of variables affecting performance
  - Fill density
  - Superpressure level
  - Application rate
  - Agent droplet size
  - Agent quality (% mass in vapor)
  - Valve, nozzle, horn design
  - Operator technique

- Design of Experiment (DOE) not applicable
- Brute force empirical approach to optimization
<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>CF₂BrCl</td>
<td>CF₃CBr=CH₂</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>0.0050</td>
<td>&lt; 20 est.</td>
<td>&lt; 20 est.</td>
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<tr>
<td>Boiling point (°C)</td>
<td>-4</td>
<td>34</td>
<td>31</td>
<td>18</td>
</tr>
<tr>
<td>Liquid density (g/cm³ @ 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 to 100,000</td>
<td>?</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></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>6.1</td>
<td>4.8</td>
</tr>
<tr>
<td>Class B MDC, % v/v</td>
<td>5.0</td>
<td>6.0</td>
<td>6.9</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>1.5</td>
<td>1.0</td>
</tr>
<tr>
<td>Relative mass efficiency, Class A</td>
<td>1.3</td>
<td>?</td>
<td>2.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Candidate 2 exhibits a mass efficiency equal to or superior to that of Halon 1211 or 2-BTP
Fire Suppression Properties of Streaming or Non-Occupied Area Agents

Mass Efficiency: Heptane Hazard

Halon 1211 = SC2 > 2-BTP > SC1

Higher mass required

Mass Efficiency: Class A Hazard

SC2 > Halon 1211 > SC1

Higher mass required
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