ABSTRACT
The hydrofluorocarbon (HFC) clean extinguishing agents are the most widely employed halon replacements worldwide, protecting billions of dollars worth of assets. This paper details the development and properties of the HFC and other halon replacements, including the requirements of the ideal halon replacement, environmental properties, toxicological properties, physical properties, fire suppression performance, environmental regulation status and applications of these agents. The HFC clean extinguishing agents provide the best combination of required properties for halon replacements, and as a result are the most widely employed halon replacements worldwide.

INTRODUCTION
This paper reviews the development of replacements for the widely employed fire extinguishing agents Halon 1301 and Halon 1211. For more than 30 years, Halon 1301 and Halon 1211 served as ideal clean fire extinguishing agents. Due to their unique combination of properties, halon systems provided protection of valuable and sensitive assets in a wide range of applications, including the protection of computer rooms, control rooms, electronic data processing facilities, museums, military installations and equipment, and oil and gas industry applications such as offshore platform and storage facility applications. However, because of their implication in the destruction of stratospheric ozone, the production and use of the halons has been severely restricted since the early 1990s. As a result, intensive research efforts were undertaken in the industrial, academic, and governmental sectors with the goal of developing replacements for the halons. This paper reviews these efforts and details the development and properties of the HFC clean agents, the most widely employed halon replacements worldwide.

HISTORIC [1]
Halogenated compounds have been employed as fire extinguishing agents since the early 1900s when handheld extinguishers containing carbon tetrachloride (CCl₄) were introduced. In the late 1920s methyl bromide (CH₃Br) was found to be more effective than carbon tetrachloride, and was widely used as a fire extinguishing agent by the British in the late 1930s in aircraft protection, and by the German military during World War II in aircraft and marine applications. Fire extinguishing systems employing bromochloromethane (CH₂BrCl) were also developed in the late 1930s and were employed by the German Luftwaffe. Bromochloromethane was evaluated in the United States during the late 1930s to the late 1940s and was eventually employed by the U.S. Air Force.

Although extremely effective as fire extinguishing agents, the relatively high toxicities of methyl bromide and bromochloromethane prompted the U.S. Army to initiate a research program to develop an extinguishing agent which retained the high effectiveness of these agents but was less toxic.
Army sponsored research at Purdue University in the late 1940s evaluated over sixty candidate agents, most of which were halogenated hydrocarbons, for both fire extinguishing effectiveness and toxicity. As a result of these studies, four agents were selected for further evaluation: bromotrifluoromethane ($\text{CF}_3\text{Br}$, Halon 1301), bromochlorodifluoromethane ($\text{CF}_2\text{BrCl}$, Halon 1211), dibromodifluoromethane ($\text{CF}_2\text{Br}_2$, Halon 1202), and 1,2-dibromo-tetrafluoroethane ($\text{BrCF}_2\text{CF}_2\text{Br}$, Halon 2402). These further evaluations eventually led to the widespread use of Halon 1301 in total flooding and small portable applications, and the use of Halon 1211 in streaming applications (portables and local application systems).

Halons 1301 and 1211 are characterized by high fire suppression efficiency, low toxicity, no residue formation following extinguishment, low electrical conductivity, and long-term storage stability. Because these agents produce no corrosive or abrasive residues upon extinguishment, they are ideally suited to protect areas such as libraries and museums, where the use of water or solid extinguishing agents could cause secondary damage equal to or exceeding that caused by direct fire damage. Because they are non-conducting they can be employed to protect electrical and electronic equipment, and because of their low toxicity they may be employed in areas where the egress of personnel may be undesirable or impossible.

Because of their unique combination of properties, the halons served as near ideal fire suppression agents during the past 30 years. However, due to their implication in the destruction of stratospheric ozone, the Montreal Protocol of 1987 identified Halon 1301 and Halon 1211 as two of a number of halogenated agents requiring limitations of use and production. An amendment to the original Montreal Protocol resulted in the halting of the production of Halon 1301 and Halon 1211 on January 1, 1994.

**HALON REPLACEMENTS**

As a result of the provisions of the Montreal Protocol, the ideal halon replacement, in addition to possessing the desirable characteristics of the halons, is required to have a much lessened environmental impact with regard to its potential for ozone depletion. The ideal halon replacement would therefore be characterized by the following properties:

- Clean (no residues)
- High fire extinguishment efficiency
- Low chemical reactivity
  - Long term storage stability
  - Noncorrosive to metals
  - High material compatibility (metals, plastics)
- Electrically non-conducting
- Low toxicity
- Zero ozone depletion potential (ODP)
- Zero global warming potential (GWP)
- Reasonable manufacturing cost

It should be noted that to date no halon replacement agent has been developed which meets all of the above requirements for an ideal halon replacement agent. Initial efforts seeking to develop viable halon replacements included the investigation of several compound classes which were later eliminated as halon replacement candidates [1]. Hydrobromofluorocarbons (HBFCs), and brominated olefins proved to be effective fire extinguishing agents, but have been eliminated from consideration due to their non-zero ODPS and relatively high toxicity. Perfluorocarbons (PFCs) are toxicologically inert and effective fire extinguishing agents, but have been banned in fire extinguishing applications due to their extremely high atmospheric lifetimes and GWPs. Iodine-containing compounds, especially iodotrifluoromethane, $\text{CF}_3\text{I}$, are extremely efficient fire extinguishing agents, but are also characterized by high toxicity, non-zero ODP and prohibitive manufacturing costs.
Four classes of compounds have emerged as commercially available halon replacements: hydrofluorocarbons (HFCs), hydrochlorofluorocarbons (HCFCs), inert gases, and perfluorinated ketones. Examples of fire extinguishing agents from each of these four chemical classes are shown in Table 1.

HALON REPLACEMENTS: CLEANLINESS

Damage to Assets. The primary characteristic of the halon agents was their “clean” nature – no corrosive or abrasive residues are left on assets or equipment following fire extinguishment with the halon agents. Traditional extinguishing agents such as water, foam or dry powder will leave a residue following extinguishment. In some cases secondary damage due the extinguishing agent can exceed the damage to assets and equipment caused by the fire itself, for example in the case of the use of water or foam type agents to extinguish fires in libraries or museums, where books, papers and other sensitive assets can be damaged by water and foam.

As seen in Table 1, HCFC Blend A contains approximately 4 percent (by weight) of the compound d-limonene. This compound, in addition to being flammable, is a high boiling liquid (boiling point 176°C). Studies [2] have shown that this high boiling liquid can be left as a residue following system discharge, e.g., inside the delivery piping system, and hence HCFC Blend A does not satisfy the essential requirement of cleanliness desired in halon replacements.

Cleanup/Business Continuity. An additional advantage of the use of clean agents is that because they leave no residues behind, there is no need for cleanup following their use. This allows for business continuity, i.e., no interruption of the services a business supplies is required following the discharge of a clean agent system. The financial impact of service disruptions can be significant, especially in telecommunications facilities and in data processing centers. The estimated downtime impact per minute for various business applications is shown in Table 2. The downtime impact for a typical computing infrastructure is estimated at $42,000 per hour. Downtime impacts for companies relying entirely on telecommunications technology, such as online brokerages or e-commerce sites, can reach $1 million per hour or more.

Table 1: Commercially Available Halon Replacements

<table>
<thead>
<tr>
<th>Designation</th>
<th>Chemical Formula</th>
<th>Trade Name</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>HFCs</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HFC-227ea</td>
<td>CF₃CHFCF₃</td>
<td>FM-200</td>
<td>DuPont</td>
</tr>
<tr>
<td>HFC-125</td>
<td>CF₃CF₂H</td>
<td>FE-25</td>
<td>DuPont</td>
</tr>
<tr>
<td>HFC-23</td>
<td>CF₃H</td>
<td>FE-13</td>
<td>DuPont</td>
</tr>
<tr>
<td>HFC-236fa</td>
<td>CF₃CH₂CF₄</td>
<td>FE-36</td>
<td>DuPont</td>
</tr>
<tr>
<td>HCFCs</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HCFC Blend A</td>
<td>CF₃HCl (82%) CF₂HCl (4.75%) CF₂CHFCl (9.5%) d-limonene (3.75%)</td>
<td>NAF-S-III</td>
<td>Safety Hi-Tech</td>
</tr>
<tr>
<td>HCFC Blend B</td>
<td>CF₃CHCl₂ CF₄Ar</td>
<td>Halotron I</td>
<td>American Pacific</td>
</tr>
<tr>
<td>Inert Gases</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IG-541</td>
<td>N₂ (52%) Ar (40%) CO₂ (8%)</td>
<td>Inergen</td>
<td>Ansul</td>
</tr>
<tr>
<td>IG-55</td>
<td>N₂ (50%), Ar (50%)</td>
<td>Argonite</td>
<td>Ginge-Kerr</td>
</tr>
<tr>
<td>IG-01</td>
<td>Ar</td>
<td>Argotec</td>
<td>Minimax</td>
</tr>
<tr>
<td>IG-100</td>
<td>N₂</td>
<td>N-100</td>
<td>Koatsu</td>
</tr>
<tr>
<td>Perfluorinated Ketones</td>
<td>FK-5-1-12</td>
<td>CF₃CF₂C(O)CF(CF₃)₂</td>
<td>Novec-1230</td>
</tr>
</tbody>
</table>

* Streaming applications (Halon 1211 replacements)
HALON REPLACEMENTS: EXTINGUISHING EFFICIENCY

With respect to fire extinguishing efficiency, the halon replacements can be separated into two classes based on their mechanism of extinguishment, inert gas agents (IGs) and halogenated agents (HFCs, HCFCs, and perfluoroketones). The inert gas agents extinguish fire via oxygen dilution, i.e., inert gas agents reduce the concentration of oxygen in an enclosure to a level where the combustion reaction rate is slowed to the point where the reaction can no longer sustain itself. The halogenated agents extinguish fire primarily via the removal of heat, i.e., the flame temperature is reduced to a temperature below that required for the maintenance of combustion. The mechanism of heat removal is a much more efficient method of fire extinguishment compared to the mechanism of oxygen dilution. As a result, the extinguishing concentrations for the halogenated agents typically range from about 4 to 12 percent via volume, compared to the inert gas agents whose extinguishing concentrations range from approximately 40 to 70 percent by volume. Table 3 demonstrates the superior efficiency of the HFC agents compared to the inert gas and perfluoroketone agents, for the representative agents HFC-227ea, IG-541, and FK-5-1-12, where it can be seen that on a mass basis less HFC-227ea is required for the extinguishment of both Class A and Class B fires compared to IG-541 and FK-5-1-12. In addition to FK-5-1-12 requiring a greater mass of agent compared to the HFCs, FK-5-1-12 is also characterized by higher cost per mass compared to the HFCs (and inert gases), rendering FK-5-1-12 systems the least cost effective of the clean agent system choices.

Table 3: Agent Quantity Required for Protection of a 100 m³ Enclosure

<table>
<thead>
<tr>
<th>Agent</th>
<th>Class A Hazard</th>
<th>Class B Hazard</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Agent required, % v/v</td>
<td>Agent required, kg</td>
</tr>
<tr>
<td>HFC-227ea</td>
<td>7.0</td>
<td>54.8</td>
</tr>
<tr>
<td>IG-541</td>
<td>40.0</td>
<td>72.4</td>
</tr>
<tr>
<td>FK-5-1-12</td>
<td>4.2</td>
<td>61.0</td>
</tr>
</tbody>
</table>

The higher volumetric requirements of the inert gas agents, along with the differing physical properties of the inert gases compared to the halocarbon agents has a significant impact on system design and cost. The inert gas agents cannot be compressed to the liquid state, and therefore must be stored as high pressure gases. This in turn necessitates the use of high pressure storage cylinders and high pressure piping for inert gas systems, adding significant cost to inert gas suppression systems. The low volumetric efficiency of the inert gas agents and their inability to be stored as liquids leads to the requirement of a large number of cylinders compared to other halon replacement systems. This in turn leads to the requirement for additional storage space and increased system footprint, adding further to the cost of the systems.
In contrast to the inert gas agents, the halogenated agents can be stored as liquids, allowing for a much larger mass of agent to be stored in a given cylinder volume compared to inert gases. This significantly reduces the number of system cylinders required with these systems compared to inert gas systems. In addition, with the exception of HFC-23, the halocarbon agents can be stored in standard low pressure cylinders and employ standard piping. Due to the requirements of high pressure piping and containers and the large number of storage containers associated with inert gas systems, system costs increase with system size much more rapidly for the inert gas systems compared to halogenated systems. Table 4 indicates the cylinder requirements for a 1000 m$^3$ Class A hazard with typical HFC (HFC-227ea), perfluoroketone (FK-5-1-12) and inert gas (IG-541) systems.

### Table 4: Halocarbon vs Inert Gas System: 1000 m$^3$ Enclosure, Class A Hazard

<table>
<thead>
<tr>
<th>Agent</th>
<th>Design Conc., % v/v</th>
<th>Agent, kg</th>
<th>Number of Cylinders</th>
</tr>
</thead>
<tbody>
<tr>
<td>HFC-227ea</td>
<td>7.0%</td>
<td>548</td>
<td>2</td>
</tr>
<tr>
<td>FK-5-1-12</td>
<td>4.2%</td>
<td>610</td>
<td>2</td>
</tr>
<tr>
<td>IG-541</td>
<td>40.0%</td>
<td>724</td>
<td>22</td>
</tr>
</tbody>
</table>

**HALON REPLACEMENTS: CHEMICAL REACTIVITY**

Halon 1301 and Halon 1211 are characterized by very low chemical reactivity, and this property is critical to the efficacy and safety of halon replacements. Chemical reactivity impacts five major aspects of halon replacement systems: system performance, agent handling, human exposure, agent cleanliness, and environmental impact. With regard to chemical reactivity, the halons, HFCs, HCFCs and inert gas agents are all characterized by very low chemical reactivity. In contrast, perfluoroketones are characterized by high chemical reactivity.

**Chemical Reactivity and System Performance.** Clean agent systems are often in place for 10 to 20 years, and must remain leak-free throughout this period. Chemical reactions producing even small amounts of acidic or corrosive products are hence undesirable, as even small amounts of such products can potentially lead to corrosion and eventual leakage of the extinguishing agent, compromising the effectiveness and safety of the extinguishing system.

Halons, HFCs, HCFCs and inert gases do not react with water or with common industrial solvents. Perfluoroketones, however, are very chemically reactive, and undergo reactions with such commonly encountered chemicals such as water, alcohols and amines. The reaction of the perfluoroketone FK-5-1-12 with water is well-documented [3-6]. Reaction of FK-5-1-12 with water produces 1,1,1,2,3,3,3-Heptafluoropropane (HFC-227ea, CF$_3$CHFCF$_3$) and Perfluoropropionic acid (F-Propionic acid, CF$_3$CF$_2$COOH):

\[
\text{CF}_3\text{CF}_2\text{C(O)CF(CF}_3\text{)_2} + \text{H}_2\text{O} \rightarrow \text{CF}_3\text{CHFCF}_3 + \text{CF}_3\text{CF}_2\text{COOH}
\]

The reaction of FK-5-1-12 with water has two major implications with regard to system effectiveness. First, system effectiveness can be affected by the loss of extinguishing agent as a result of chemical reaction - any amount of agent undergoing chemical reaction is not available for extinguishment. Indeed, perfluoroketone FK-5-1-12 (Novec 1230) design manuals advise that “contact with water or solvents either polar or hydrocarbon could render Novec 1230 ineffective”[3]. Secondly, the production of corrosive compounds due to chemical reaction can lead to corrosion of the system cylinders and leakage of agent. As indicated above, the reaction of FK-5-1-12 with water produces F-Propionic acid [3-6]. F-Propionic acid is a highly toxic and corrosive acid [7]. It belongs to the class of perfluorocarboxylic acids (PFCAs), which are among the strongest acids known. F-Propionic acid
attacks steel to produce the corresponding iron salt; the formation of this salt in FK-5-12 cylinders exhibiting signs of corrosion has been verified [8]. F-Propionic acid is also toxic, and is reported to cause eye and skin burns, damage to the digestive tract, and gastrointestinal burns [7]. PFCAs as a class are known tumor promoters causing damage to the liver [9]. Effects on the liver and lungs following exposure to FK-5-1-12 have been observed [6].

Chemical Reactivity and Agent Handling. Halons, HFCs, HCFCs and inert gases do not react with water, and hence no special procedures are required when handling these agents to avoid the introduction of water. Perfluoroketones, in contrast, are known to undergo reaction with water, and hence special procedures are required when handling these agents to avoid the introduction of moist air into the product. As a result, perfluoroketone FK-5-1-12 (Novec 1230) design manuals prescribe special handling procedures such as the use of vent driers and nitrogen purges to prevent contact of perfluoroketone with moist air [3, 5].

Chemical Reactivity and Human Exposure. The ideal halon replacement does not react within the human body, i.e., the ideal halon replacement is not metabolized. The HFCs employed as clean agents, and the inert gas clean agents, are not metabolized within the human body and do not react with water. Perfluoroketones, in contrast, undergo reaction with water, and FK-5-1-12 is hydrolyzed when it crosses the lung-air interface to produce HFC-227ea and F-Propionic acid [4].

Chemical Reactivity and Cleanliness. Chemical reactivity is also undesirable due to potential implications related to the cleanliness of the extinguishing system. Chemical reaction of the extinguishing agent with enclosure contents runs counter to the purpose of a “clean” extinguishing system. Halons, HFCs, and inert gas agents are chemically unreactive, and hence do not pose a threat to protected assets. Due to their high chemical reactivity, perfluoroketones can undergo reaction with certain materials. Figure 1 shows the results of the discharge of FK-5-1-12 in an enclosure lined with FRP fiber-reinforced polymer cladding, where it can be seen that staining of the FRP cladding results; identical exposure to HFC or inert gas agents does not produce any effects on the cladding.

Chemical Reactivity and Environmental Impact. Chemical reactivity also has an impact on the environmental impact of extinguishing agents. The HFCs are chemically stable, and hence their atmospheric fate is not complicated by chemical reactions such as hydrolysis. It is well established that HFCs undergo reaction with hydroxyl radicals in the troposphere and the ultimate products are well understood. In the case of FK-5-1-12, however, the current GWP value is based solely on the photolysis of perfluoroketones, and does not take into account potential reactions with water in the atmosphere, which in the case of FK-5-1-12 would produce HFC-227ea and F-Propionic acid.

Figure 1: FK-5-1-12 Discharge onto FRP Cladding
HALON REPLACEMENTS: ENVIRONMENTAL PROPERTIES

The environmental properties of the halon replacements are compared in Table 5. The inert gas agents afford the minimum environmental impact, as evidenced by their ODP and GWP values. The use of these systems is limited, however, due to a number of factors as discussed above, e.g., the requirement of high pressure cylinders and piping, the large number of cylinders required and the resulting large system footprint and system cost. The halons have already been phased out, and HCFC-based agents are scheduled for phase-out, due to their non-zero ODP. The GWP of the perfluoroketones is reported to be low, however, as discussed above, this analysis does not take into account the potential reaction of perfluoroketones with atmospheric water, which could significantly affect the GWP and ultimate environmental impact of this class of agents.

Table 5: Environmental Properties of Halon Replacements

<table>
<thead>
<tr>
<th></th>
<th>Halon 1301</th>
<th>HFC-227ea</th>
<th>HCFC Blend A</th>
<th>IG-541</th>
<th>FK-5-1-12</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition</td>
<td>CF₃Br</td>
<td>CF₃CHFCF₃</td>
<td>HCFC-22</td>
<td>N₂</td>
<td>CF₂CF₂C(O)CF(CF₃)₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>HCFC-123</td>
<td>Ar</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>HCFC-124</td>
<td>CO₂</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>d-limonene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ODP</td>
<td>10</td>
<td>0</td>
<td>&gt;0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>GWP</td>
<td>6900</td>
<td>3140</td>
<td>1700</td>
<td>CO₂ = 1</td>
<td>1*</td>
</tr>
<tr>
<td>Atmospheric</td>
<td>65</td>
<td>34</td>
<td>12</td>
<td></td>
<td>0.014</td>
</tr>
<tr>
<td>lifetime (yr)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Scheduled for</td>
<td>PHASED</td>
<td>NO</td>
<td>YES</td>
<td>NO</td>
<td>NO</td>
</tr>
<tr>
<td>Phase-out?</td>
<td>OUT</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Neglects reaction of FK-5-1-12 with water

HALON REPLACEMENTS: ENVIRONMENTAL REGULATIONS

Montreal Protocol. The Montreal Protocol is related to ozone depleting substances (ODSs), i.e., substances with non-zero ODPs. The Halons have been phased out under the requirements of the Montreal Protocol, and the HCFCs are scheduled for phase-out under the requirements of the Montreal Protocol. HFCs, inert gases, and perfluoroketones are characterized by zero ODPs, and hence are not subject to the provisions of the Montreal Protocol.

Kyoto Protocol. The sole intent of the Kyoto Protocol is to reduce the emissions of greenhouse gases (GHGs). The Kyoto Protocol neither proposes nor requires the limitation or banning of GHGs, but only calls for measures to be taken to reduce GHG emissions. Hence, the Kyoto Protocol does not place any limitations or bans on the use of GHGs, including HFCs, in fire extinguishing applications.

F-Gas Regulations. Like the Kyoto Protocol, the F-Gas Regulation is primarily concerned with the reduction of GHG emissions. The F-Gas Regulations neither propose nor require any limitations or bans on the use of HFCs in fire extinguishing applications. International regulations such as the Kyoto Protocol and the F-Gas Regulations recognize the essentially non-emissive nature of clean agent systems, the critical need for HFCs in fire extinguishing applications, and the extremely small contribution to climate change due to the use of HFCs in fire extinguishing applications. It has been estimated that the total impact of HFC emissions represents less than 3 percent of the impact of all GHG emissions, and that the impact of HFC emissions from fire fighting represents less than 1 percent of the total impact of all HFC emissions [10, 11]. Hence, the impact of HFC emissions from fire fighting represents less than 0.03% of the impact of all total global GHG emissions. Figure 2 shows the relative contribution of the various GHGs in terms of Mtons of carbon dioxide equivalents, where it can be seen that the impact of GHG emissions from the use of HFCs in fire fighting is miniscule.
HALON REPLACEMENTS: TOXICOLOGY

Inert gas toxicity is due primarily to asphyxiation (low oxygen level) at elevated inert gas concentrations, i.e., at inert gas concentrations exceeding approximately 43% v/v. The toxicological properties of HFCs and perfluoroketones are compared in Table 6. As seen from Table 6, the HFC agents are the least toxic of the agent types listed, being characterized by very low acute and chronic toxicity, and a lack of metabolism within the human body. HFC-227ea is characterized by extremely low acute and chronic toxicity, and has been approved by the US Food & Drug Administration for use as a propellant for metered dose inhalers, in which the HFC-227ea is used to propel a medicament down the patient’s throat. The toxicology of perfluoroketones is a virtually unexplored area. Hexafluoropropionate (perfluoropropionate), the parent compound of the perfluoroketone class, is an extremely toxic material [12], and toxicological studies have been reported for only one other perfluoroketone, FK-5-1-12. Unlike the HFCs which are not metabolized, FK-5-1-12 is metabolized. FK-5-1-12 reacts with water [3-6] forming HFC-227ea and the corrosive, toxic acid F-Propionic acid upon crossing the lung-air interface, and effects on the liver and lung have been observed [6].

Table 6: Toxicological Profile: HFCs and Perfluoroketones

<table>
<thead>
<tr>
<th></th>
<th>HFC-227ea</th>
<th>HFC-125</th>
<th>FK-5-1-12</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inhalation LC50 (4h, rat)</td>
<td>&gt; 80%</td>
<td>&gt; 80%</td>
<td>&gt; 10%</td>
</tr>
<tr>
<td>Cardiac Sensitization NOAEL</td>
<td>9.0%</td>
<td>7.5%</td>
<td>10%</td>
</tr>
<tr>
<td>Cardiac Sensitization LOAEL</td>
<td>&gt; 10.5%</td>
<td>10.0%</td>
<td>&gt; 10%</td>
</tr>
<tr>
<td>PBPK Safe level</td>
<td>10.5%</td>
<td>11.5 %</td>
<td>PBPK data not available</td>
</tr>
<tr>
<td>Repeated Dose Inhalation (28 bay, rat)</td>
<td>NOAEL &gt; 5.0%</td>
<td>NOAEL &gt; 5.0%</td>
<td>LOAEL = 0.0997%</td>
</tr>
<tr>
<td>Metabolism</td>
<td>Negligible</td>
<td>Negligible</td>
<td>Hydrolyzes to F-Propionic acid</td>
</tr>
</tbody>
</table>

NOAEL = no observed adverse effect level; LOAEL = lowest observed adverse effect level

* 90 day study

* NICNAS Std/1019 [Reference 5]
HALON REPLACEMENTS: OVERALL COMPARISON

The above discussions have compared the properties of commercially available halon replacements with respect to five critical characteristics: fire extinguishment efficiency, cleanliness, chemical reactivity, environmental properties and toxicological properties. Table 7 provides a summary comparison of the halon replacements in terms of these and additional desired properties of the ideal halon replacement. As seen from Table 7, no agent satisfies all of the requirements of the ideal halon replacement; however, it can be seen from the table that the HFCs represent the best overall combination of the desired properties. The halons and HCFCs both meet a large portion of the desired requirements, but have been phased out (in the case of the halons), or will be phased out (in the case of the HCFCs) due to their non-zero ODPs. It can also be seen from Table 7 that the agent class offering the second best combination of desired properties (after the HFCs) is the inert gases. As discussed in the next section, this is exactly how the clean agent market has developed worldwide – HFCs are the most widely employed halon replacements, followed by the inert gas agents.

Table 7: Overall Comparison of Halon Replacements

<table>
<thead>
<tr>
<th>Ideal Halon Replacement</th>
<th>Halon 1301</th>
<th>HFCs</th>
<th>HCFCs</th>
<th>Inert Gases</th>
<th>F-ketones</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zero ODP</td>
<td></td>
<td></td>
<td></td>
<td>x</td>
<td></td>
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<td>High Weight Efficiency</td>
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<td>Cleanliness</td>
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<tr>
<td>Low Chemical Reactivity</td>
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<tr>
<td>Low Toxicity</td>
<td>x</td>
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<tr>
<td>Low Metabolism</td>
<td>x</td>
<td>x</td>
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<td>Low Agent Cost</td>
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<td>Low System Cost</td>
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<td>Ease of Gasification</td>
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<td>Low No. Cylinders</td>
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<td>Low System Footprint</td>
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<td>Low Manifold pressure rating</td>
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<td>Slow Stratification</td>
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<td>Low Enclosure pressures</td>
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<tr>
<td>Zero GWP</td>
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HALON REPLACEMENTS: MARKET & APPLICATIONS

Figure 3 shows the breakdown of the global clean agent market by agent type. HFC systems account for approximately 70% of all installed clean agent systems globally; inert gas systems account for approximately 20% of the total market, and other agents represent approximately 10% of the total installed clean agent systems.
As seen in Figure 4, two agents, HFC-227ea (FM-200®) and IG-541 (Inergen®) are most favored in the global halon replacement market. Together they account for approximately 90% of installed clean agent systems. HFC-227ea is the most widely employed Halon 1301 replacement worldwide, and is also the most tested clean agent. It is estimated that there are approximately 300,000 HFC-227ea systems installed worldwide, in more than 65 countries. HFC-227ea systems have been installed beginning in 1991, and hence there exist 17 years of experience with these HFC clean agents systems, during which time the systems have demonstrated their safety and performance.
Applications of the HFC clean agents include the classic Halon 1301 applications: telecommunication facilities, computer rooms, data centers, museums, libraries, hospitals, medical facilities, medical equipment, clean rooms, engine compartments, engine nacelles, petrochemical facilities, grain elevators, oil rig platforms, floating roof tanks, and aircraft.

Table 8 lists a number of facilities worldwide which employ HFC clean agent systems, and Figure 6 lists a selection of the numerous industry leaders which employ the HFC clean agent systems. It can be seen from these tables that the HFC agents have been widely accepted on a global basis.

<table>
<thead>
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<th>Table 8: Select Applications of the HFC Clean Agents</th>
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<tr>
<td>American Museum of Natural History</td>
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<td>Smithsonian Institute</td>
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<td>Library of Congress</td>
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<td>Alexandria Library, Egypt</td>
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<td>Royal Thai Silk Museum, Thailand</td>
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<td>North American DEW Line Radar Installation</td>
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<td>Dusseldorf Airport</td>
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<td>San Francisco Airport</td>
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Figure 6: Industry Leader Acceptance of HFC Clean Agents
CONCLUSION
The HFC clean agents provide the best overall combination of the properties desirable in a clean agent replacement for the halons: high effectiveness, cleanliness, low chemical reactivity, low toxicity, minimal environmental impact, and competitive system cost. As a result, the HFCs are the most widely employed halon replacements worldwide, and these systems currently protect billions of dollars worth of assets in more than 65 countries. HFC clean agent technology is a mature technology, having provided protection of valuable assets for over 17 years with an excellent performance and safety record.

REFERENCES


2. Robin, M.L.and Rowland, T.F., Great Lakes Chemical Corporation internal report.


7. Perfluoroproponic acid MSDS.


12. Hexafluoroacetone MSDS.