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Advances in Clean Agents for Fire Protection

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Clean Agents in Total Flooding Applications

By
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Up until the early 1990s, the choice of a clean agent for a total flooding application was relatively simple, as the clean agent market consisted of only two agents: Halon 1301 (CF_3Br) and carbon dioxide (CO_2). Carbon dioxide systems have been employed for more than a century and have extinguished more fires than any other gaseous fire extinguishing agent. However, the minimum design concentration for CO_2 total flooding systems is 34 percent by volume, well above the acceptable exposure threshold for personnel. As a result, NFPA 12 prohibits the use of total flooding CO_2 systems in normally occupied spaces with specific exceptions, and where a gaseous total flooding system was desired for a normally occupied enclosure, Halon 1301 was generally recommended.

Due to its unique combination of chemical and physical properties, Halon 1301 served as a nearly ideal fire suppression agent for over 30 years. However, due to its implication in the destruction of stratospheric ozone, the Montreal Protocol of 1987 identified Halon 1301 as one of numerous compounds requiring limitations of use and production, and an amendment to the original Protocol resulted in the halting of Halon 1301 production in developed countries on December 31, 1993; there is currently no production of Halon 1301 for use in fire suppression applications.

Halon 1301 Replacements

Commercialized Agents

Out of the thousands of compounds evaluated as replacements for the halons, less than a dozen compounds ever saw commercialization. Five classes of compounds ultimately emerged as commercially available halon replacements: hydrofluorocarbons (HFCs), hydrochlorofluorocarbons (HCFCs), inert gases, perfluorocarbons (PFCs) and a perfluorinated ketone (PFK). The perfluorocarbon agents were banned from use in fire suppression in the early 1990s due to their extremely long atmospheric lifetimes and permanent effect on climate change. The HCFC agents are slated for phaseout due to their non-zero ODPs and are transitional replacement agents only.

Table 1 shows the currently available Halon 1301 replacements. Halon 1301 replacements can be separated into two classes based on their mechanism of fire extinguishment: inert gas agents and halogenated agents (HFCs, HCFCs, and perfluoroketone). The inert gas agents extinguish fire via oxygen dilution, whereas the halogenated agents extinguish fire primarily via the removal of heat. On a volumetric basis, 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 by volume, compared to the inert gas agents whose extinguishing concentrations range from approximately 40 to 70 percent by volume. On a mass basis, the HFC agents are more efficient than the inert gases or the perfluoroketone. Table 2 provides a comparison of agent requirements on a mass and volume basis for FM-200®, Inergen® and Novec™ 1230.

Table 1. Commercially Available Halon 1301 Replacements

	Designation	Chemical Formula	Trade Name	Manufacturer
HFCs	HFC-227ea	CF_3CHFCF_3	FM-200®	DuPont
	HFC-125	CF_3CF_2H	FE-25™	DuPont
	HFC-23	CF_3H	FE-13™	DuPont
HCFCs	HCFC Blend A	CF_2HCl (82%) CF_3CHCl_2 (4.75%) CF_3CHFCl (9.5%) d-limonene (3.75%)	NAF-S-III®	Safety Hi-Tech
Inert Gases	IG-541	N_2 (52%) Ar (40%) CO_2 (8%)	Inergen®	Ansul
	IG-55	N_2 (50%), Ar (50%)	Argonite™ Proinert®	Ginge-Kerr Fike Corp.
	IG-01	Ar	Argotec	Minimax
	IG-100	N_2	NN100	Koatsu
Perfluorinated Ketone	FK-5-1-12	$CF_3CF_2C(O)CF(CF_3)_2$	Novec™ 1230	3M

Table 2. Agent Requirements: NFPA 2001 (2012 Edition)

Agent	**Class A Hazard**		**Class C Hazard**	
	Minimum Design Conc., % v/v	Agent required per 1000 ft^3, lb	Minimum Design Conc., % v/v	Agent required per 1000 ft^3, lb
FM-200®	6.7	32.5	7.0	34.1
Inergen®	34.2	36.9	38.5	42.8
Novec™ 1230	4.5	40.7	4.7	42.6

Comparison of Inert Gases and Halocarbons

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 the same 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

The Ideal Halon 1301 Replacement

The ideal Halon 1301 replacement, in addition to possessing the desirable characteristics of Halon 1301, is required to have a much lessened environmental impact with regard to its potential for ozone depletion, and also with regard to its potential for contributing to climate change. 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)
  - No effect on biological tissues
- Electrically non-conducting
- Low toxicity
- Zero ozone depletion potential (ODP)
- Zero global warming potential (GWP)
- Reasonable manufacturing cost

To date no replacement agent has been found which satisfies all of the above requirements, although replacements have been found that match many of the above criteria. Each class of extinguishant has strengths and weaknesses, and agent selection must be based on the criteria listed above along with detailed knowledge of the specific project requirements.

A summary comparing the qualitative differences between the clean agent extinguishant classes relative to Halon 1301 is found in Table 3. As seen from the table, no agent satisfies *all* of the requirements of the ideal halon replacement; however, it can be seen from the table that the HFCs, followed by the inert gas agents, provide the best overall combination of desired properties.

In line with the characteristics of the various clean agents, the clean agent marketplace is dominated by two agents: the HFC agent FM-200® followed by the inert gas agent Inergen®. The Novec™ 1230 perfluoroketone agent differs from Halon 1301 and all other Halon 1301 replacements in three key aspects: chemical reactivity, effect on biological tissues and physical state. Unlike the HFC and inert gas clean agents, which are characterized by very low chemical reactivity, Novec™ 1230 is characterized by high chemical reactivity. The reaction of Novec™ 1230 with water produces HFC-227ea and Perfluoropropionic acid, a strong, corrosive organic acid. Due to its high reactivity, Novec™ 1230 is the only clean agent that is classified as a volatile organic compound (VOC).

Table 3. Comparison of Clean Agent Classes

Ideal Halon Replacement	Halon 1301	HFCs	Inert Gases	Perfluoroketones
Gaseous agent	√	√	√	
Low chemical reactivity	√	√	√	
No effect on biological tissues	√	√	√	
Electrically nonconducting	√	√	√	√
High weight efficiency	√	√	√	
Low agent cost	√	√	√	
Low system cost	√	√	√	
Low storage volume	√	√		√
Low number cylinders	√	√		√
Low cylinder pressure	√	√		√
Low manifold pressure	√	√		√
Low enclosure pressure	√	√		√
Zero ODP		√	√	√
Zero GWP			√	
Non-VOC	√	√	√	

Unlike the HFC and inert gas agents, Novec™ 1230 undergoes reaction in the lungs, to form HFC-227ea and Perfluoropropionic acid when it crosses the lung-air interface. In contrast, the HFC and inert gas agents do not react to form potentially hazardous products. The toxicity of FM-200® is so low that it is approved for use as a propellant in metered dose inhalers (MDIs), where it is employed to propel a medicament down the throat of the patient into his/her lungs.

Unlike the HFC and inert gas clean agents, which are all gaseous at room temperature, Novec™ 1230 is a high boiling liquid (bp = 48 °C). This increases the possibility of a liquid discharge with Novec™ 1230 compared to the other clean agents and also affects its performance. For example, recent studies have indicated that Novec™ 1230 is ineffective in several civil aviation applications.

Clean Agent Applications

Clean agents are employed in a myriad of applications, including pleasure boats, marine and military vessels, flight simulators, medical facilities, cellular sites, internet service provider (ISP) centers, TV and radio control rooms, microwave relay towers, anechoic test chambers, clean rooms, flammable liquid storage areas, art galleries, libraries and museums. Worldwide, numerous high value items are protected by clean agent systems. FM-200® suppression systems protect the electrical systems of the Eiffel Tower, the first draft of the Declaration of Independence, and protected the Star Spangled Banner during its recent restoration. Inergen® systems protect copies of the Gettysburg Address, copies of the Gutenberg Bible, and paintings by Picasso and Monet. FE-25™ suppression systems protect the engine nacelles of the U.S. Navy F/A-18E/C and V-22 aircraft, and FE-13™ systems are employed in inerting applications on the North Slope and McMurdo Station in Antarctica.

Clean Agents in the Future

With the expected future increase in the reliance of businesses on expensive, sensitive and mission-critical equipment such as computers and electronic equipment, the need for clean agent fire protection is also expected to experience vigorous growth. The HFC clean agents, followed by the inert gas agents have been proven to provide the best overall combination of the properties desired in a clean agent replacement for Halon 1301 and it is expected that these agents will continue to dominate the clean agent marketplace.

Future Regulation of Clean Agents in Fire Suppression Applications

With regard to the regulation of any chemical, no one can guarantee a lack of future regulations, and speculation on this point serves only to confuse the industry and drive end users to non-clean alternatives such as sprinklers. No one can guarantee that HFCs in fire suppression applications will never be phased out - not without being able to divine the future. Can anyone guarantee that perfluoroketones will not be phased out in the future? Unlike all other clean agents, perfluoroketones are characterized by high chemical reactivity (e.g., hydrolysis when crossing the lung-air interface to form perfluoropropionic acid, cf. Novec™ 1230 Fire Protection Fluid Safety Assessment, 3M). Because of this effect of Novec™ 1230 on biological tissues, facility managers are expressing increasing concern over the ultimate safety in use of perfluoroketones in normally occupied areas.

Even the inert gases have been challenged by acoustic damage, high cylinder pressures, and room over-pressurization. Regulations continuously evolve as new science, information, and issues develop in the marketplace and no product is immune to a changing regulatory future.

No other issue related to clean agents is perhaps more misunderstood and misrepresented in the marketplace than the issue of the environmental impact of HFCs in fire suppression applications. Two oft-encountered examples of such misinformation are the assertions that the emissions of HFCs in fire suppression applications are rapidly growing, and that as a result, the impact of HFCs in fire suppression applications on climate change is rapidly increasing. Factual data available from third part sources indicates otherwise. Table 4 provides a summary of US EPA estimates of the impact of HFCs in various applications on climate change from 2005 to 2010, the latest date for which data is currently available. As seen from Table 4, the contribution of HFCs in fire suppression applications to climate change has remained essentially constant over this period, despite growth of the HFC clean agent market. The contribution of HFCs in fire suppression applications to climate change is minuscule, representing only 0.01% of the impact of all GHGs on climate change.

Table 4. Impact of Emissions of HFCs from Fire Suppression Applications on Climate Change: Historical

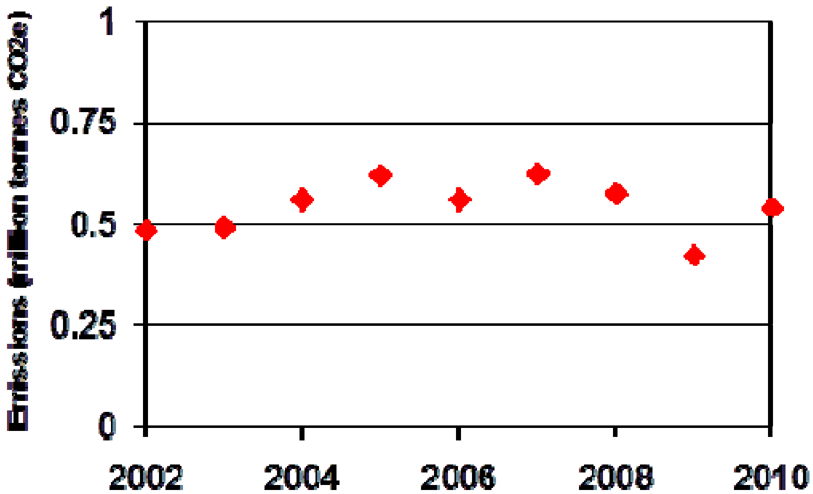
	Tg of Carbon Dioxide Equivalents					
	2005	2006	2007	2008	2009	2010
Refrigeration/AC	87.9	90.1	90.3	90.4	91.3	97.6
Aerosol	7.3	7.7	8.2	8.6	9.1	9.3
Foam	1.9	2.1	2.3	2.5	3.9	5.4
Solvent	1.3	1.3	1.3	1.3	1.3	1.3
Fire Protection	0.5	0.6	0.7	0.7	0.8	0.9
Semiconductor manufacture	0.2	0.3	0.3	0.3	0.3	0.3
R-22 manufacture	15.8	13.8	17	13.6	5.4	8.1
Total HFCs	114.9	115.9	120.1	117.4	112.1	123.0
Total All GHGs	7204.3	7159.2	7252.8	7048.4	6608.3	6821.7
Contribution to climate change from HFCs in fire extinguishing applications	0.01%	0.01%	0.01%	0.01%	0.01%	0.01%

Source: Inventory of US GHG Emissions & Sinks: 1990-2010 (US EPA, 4/15/2012)

Estimates of emissions of HFCs from fire protection applications from the US EPA and EU-15 countries are consistent with the emission estimates from the HFC Emissions Estimating Program (HEEP); as seen in Figure 1, HEEP data also indicate that the emissions of HFCs from fire suppression application are not increasing but have remained essentially steady for the past decade.

It is a fact, that with regard to regulations, HFCs in fire suppression applications are being treated differently than HFCs employed in other applications. Emissions of HFCs from fire suppression applications are dwarfed by HFC emissions from other applications such as refrigeration. Regulatory bodies understand this, and to date HFCs in fire suppression applications have been subject to different sets of regulations. A good example is the F-Gas regulation in Europe, which has adopted, supported and regulated good industry practices around system filling, handling, and servicing of fire systems.

Figure 1. Fire Extinguishing Emissions of HFCs:
HFC Emissions Estimating Program (HEEP)



Source: HARC (2012)

CONCLUSION

Clean agents are ideally suited for the protection of sensitive, expensive and mission-critical assets, and are employed to protect billions of dollars worth of assets worldwide. With the demise of the halons, extensive efforts have been undertaken in the past 25 years to develop "Son of Halon" involving the screening and evaluation of thousands of candidates. However, to date no replacement has been found which meets all of the criteria of the ideal halon replacement. As a result, agent selection must be based on consideration of all the key criteria of a Halon 1301 replacement along with detailed knowledge of the specific project requirements. The HFC clean agents, followed by the inert gas agents have been proven to provide the best overall combination of the properties desired in a clean agent replacement for the halons: high effectiveness, cleanliness, low chemical reactivity, low toxicity, minimal environmental impact, and competitive system cost. With the expected future reliance of businesses on expensive, sensitive and mission-critical equipment such as computers and electronic equipment, the need for clean agent fire protection is also expected to experience vigorous growth.