SHORT COURSE

Commercialized Halon Options*

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Introduction

In 1987, an international treaty—the Montreal Protocol—was established to control the release of materials that cause stratospheric ozone depletion. Under the Protocol, the production of halon fire and explosion protection agents was phased out in all industrialized countries at the end of 1993. To date, no environmentally acceptable halon replacement equivalent to the existing halons in toxicity, effectiveness, and dimensionality across all applications has been identified. A large number of new agents and technologies that provide adequate protection in most applications (usually, with tradeoffs) have, however, been developed.

This paper presents an overview of halon options that have been commercialized or are near to commercialization.[†] The term "options" is used here for anything that could be used in place of halons. There are two types of options: (1) "replacements" are halocarbon agents chemically similar to the present halons; (2) "alternatives" are everything else. "Chemical alternatives" are materials such as carbon dioxide, foam, water, and dry chemical, which are chemically distinct from the halons. "Engineering alternatives" (not covered here) refer to approaches such as rapid response and fire resistant structures.

Halon Fire Extinguishants

Halon fire extinguishing agents are low boiling point halocarbons (chemical compounds that contain carbon and one or more of the halogen elements—fluorine, chlorine, bromine, and iodine) that have been extensively used in the past to suppress fires and to protect against explosions (Table 1).[‡]

TABLE 1. HALON FIRE AND EXPLOSION PROTECTION AGENTS.

Halon No.	Halocarbon No.	Chemical Name	Formula	Boiling Pt., °C
Halon 1301	BFC-13B1	bromotrifluoromethane	$CBrF_3$	-58
Halon 1211	BCFC-12B1	bromochlorodifluoromethane	$CBrClF_2$	-3
Halon 2402	BFC-114B2	1,1-dibromotetrafluoroethane	$CBrF_2CBrF_2$	47

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[*] A number of commercial products (requiring Trademark ® or ™) are mentioned in this paper. Because of the frequency of usage, Trademarks are not indicated.

[†] For a continuing update on halon options, see the International Halon Replacement Working Group website at http://nmeri.unm.edu/cget/ihrwg.htm.

[‡] The term "halon" can be applied to any halocarbon fire extinguishing agent. In this paper, however, "halon" is used only to denote Halons 1211, 1301, and 2402.

There are four general types of fire and explosion protection applications for halons. (1) In total-flooding applications, the agent is discharged into a space to achieve a gas or vapor concentration sufficient to extinguish or suppress an existing fire. This is often done by an automatic system, which detects the fire and then automatically discharges. (2) In streaming applications, the agent is applied directly onto a fire or into the region of a fire. This is normally accomplished using manually operated portable units. **(3)** In explosion suppression, a halocarbon is discharged to suppress an explosion that has already been initiated. **(4)** In inertion, a halocarbon is discharged into a space to prevent an explosion or a fire from occurring. The last two applications (explosion suppression and inertion) often **use** systems similar or identical to those used for total-flooding fire extinguishment and can be considered to be total-flooding applications (as done for convenience in this paper). There are, however, some differences. For example, explosion suppression performance appears to be highly dependent on heat absorption by the discharged agent, whereas fire suppression appears to be highly dependent on interference by an agent in the chemistry **of** a fire.

Halon 1301 is typically used in total-flooding applications, and Halon 1211 is usually used in streaming (in Europe, Halon 1211 is also often used in total-flooding and similar systems). There are two reasons for **this.** First, Halon 1301 has a very low boiling point and discharges from a nozzle **as** a gas, which allows rapid filling of an enclosed area. With its higher boiling point, Halon 1211 discharges as a mixture of gas and liquid, which allows streaming over longer distances from a nozzle. Second, the toxicity **of** Halon 1301 is lower than that of Halon 1211, which allows use with the higher exposure levels typical of total-flooding systems.

Commercialized Replacements

Chemical Families

At present, halon replacements (e.g., halocarbons) fall into four major classes of compounds (Table 2). Two additional classes of replacement agents that had a short use in the past—CFCs (chlorofluorocarbons) and HBFCs (hydrobromofluorocarbons)—are no longer commercialized as halon replacements.

TABLE 2. CLASSES OF HALON REPLACEMENTS.

HCFC	Hydrochlorofluorocarbons
FC (PFC)	Perfluorocarbons
HFC	Hydrofluorocarbons
FIC	Fluoroiodocarbons

A number of characteristics **are** desirable for replacement agents. They must, of course, have acceptable environmental characteristics. Of particular importance is the requirement for a low impact on stratospheric ozone and global warming. The toxicity must also be acceptable, though there may be some debate about what is acceptable. The primary reason for using halocarbons, rather than such alternatives as foams and dry chemicals, is that halocarbons are clean, volatile, and electrically non-conductive. Finally, the agent must be effective. Note, however, that effectiveness does not necessarily mean as effective as the present halons, though this is desirable.

Physical action agents (PAA) are those that operate primarily by heat absorption. Chemical action agents (CAA) are those that operate primarily by chemical means. In general, CAAs are much more effective extinguishants than are PAAs. Halons 1211 and 1301 are primarily CAAs. Though CAAs are more effective, they often have an unacceptable environmental impact because they often contain bromine. One exception is trifluoroiodomethane, CF_3I, which is the only CAA being commercialized today.

Environmental Characteristics

Three environmental characteristics are of particular interest in assessing halon replacements. (1) The Ozone Depletion Potential (ODP) is a measure of the ability of a chemical to deplete stratospheric ozone. ODPs are the calculated ozone depletions per unit mass of material released relative to a standard, usually CFC-11. *(2)* The Global Warming Potential (GWP) of a chemical is the change in global warming caused by release of a chemical relative to that resulting from release of a reference gas (now, usually carbon dioxide). (3) The atmospheric lifetime gives the persistence of a chemical in the atmosphere. Atmospheric lifetime is of increasing concern, in part due to the potential for global warming. Global warming usually increases as the atmospheric lifetime increases (though there are exceptions). There is, however, also concern about unanticipated effects of a chemical lasting for many years in the atmosphere. Both ODPs and GWPs and atmospheric lifetimes are calculated; they cannot be measured.

HCFCs have much lower impact on stratospheric ozone than do the halons. Nevertheless, this impact is not zero, and, for this reason, the production of these chemical agents will eventually be phased out. Some restrictions are already in place in parts of Europe (and to a limited extent in the USA). The European Community (EC) regulation 3093/94, entered into force 1 June 1995, bans the use of HCFCs for fire protection.

PFCs are fully fluorinated compounds, unlike HCFCs or HFCs, and have several attractive features. They are nonflammable, have a low toxicity, and do not contribute to stratospheric ozone depletion. The environmental characteristics of concern, however, is their large impact on global warming and their long atmospheric lifetimes.

HFCs are receiving increased prominence as replacements for ozone depleting substances because they are not ozone depleting as are the HCFCs and because they have lower atmospheric lifetimes than PFCs. There is, however, still considerable concern about the contribution of HFCs to global warming.

Toxicological Characteristics

Cardiac sensitization is usually the first toxicological effect observed during acute exposures by inhalation to halocarbons. Cardiac sensitization refers to a sudden onset of cardiac arrhythmias (irregular heartbeats) caused by a sensitization of the heart to epinephrine (adrenaline). The lowest exposure level that has been observed to cause an adverse effect is termed the “Lowest Observed Adverse Effect Level” (LOAEL), and the highest exposure level that has been found to cause no adverse effect is termed the “No Observed Adverse Effect Level” (NOAEL).

In the United States, two slightly different sets of toxicological restrictions have been established for total-flooding protection. The 1996 NFPA (National Fire Protection Association) Standard 2001 [1] requires that the design concentration for total flooding of a normally occupied area by halocarbons not exceed the cardiac sensitization NOAEL. As an exception, a halocarbon agent may be used up to the LOAEL value for Class B (liquid fuel fire) hazards in normally occupied areas where a predischarge alarm and time delay are provided. The time delay must be set to ensure that occupants have time to evacuate prior to the time of discharge. In addition, halocarbon agent concentrations above 24% are not allowed in normally occupied areas.*

The U. S. Environmental Protection Agency (US EPA) applies the following: (1) Where egress from an area cannot be accomplished within 1 min, the agent concentration cannot exceed the NOAEL. (2) Where egress takes longer than 30 sec but less than 1 min, the agent concentration cannot exceed the LOAEL. **(3)** Agent concentrations greater than the LOAEL are only permitted in areas not normally occupied by employees provided that any employee in the area can escape within 30 sec. Thus, unlike the NFPA, the US EPA applies specific time limits for evacuation from areas where a total-flooding discharge is used.

The New Extinguishants Advisory Group (NEAG), a subgroup of the Halon Alternatives Group (HAG) in the **U.K.,** has attempted to base allowable design concentrations for automatic total-flooding fire suppression systems in occupied areas on six endpoints: LC_{50}, Central Nervous System (CNS) effects, cardiac sensitization, respiratory sensitization, genotoxicity, and developmental toxicity [2]. For the three halocarbon agents that they evaluated, NEAG found that cardiac sensitization or, for very low-toxicity agents, hypoxia (adverse health effects due to low oxygen levels) is the critical endpoint.

Commercialized Halon Replacements

Halon replacements being commercialized for total-flooding applications are shown in Table **3,** and the design concentrations **for** fire extinguishment are shown in Table 4. These design concentrations are minimum manufacturer-recommended values for extinguishment of n-heptane fuel fires. Design concentrations may differ **for** other fuels and will be higher for inertion **of** an area. Some users are employing agents at considerably higher concentrations than the minimum recommended values based on the specific fuel, scenario, and threat. The new draft International Standards Organization **(ISO)** standard **[3]** calls for larger design concentrations than shown in Table **4** for some agents. Table 4 also gives the NOAEL and LOAEL toxicity levels for commercialized total-flooding agents. Some of these agents cannot be used for total flooding in occupied areas under NFPA Standard 2001 criteria [1], with the exception of Class B fires with a predischarge alarm and a time delay. Table **5** gives the global environmental characteristics of agents commercialized for total-flood applications. The ODPs are relative to CFC-11 and the GWPs (calculated for a 100-yr time horizon) are relative to CO_2.

Table **6** gives lists those agents being commercialized for streaming, and Table 7gives toxicological data. With the possible exception of FIC-13I1, none of the streaming agent candidates appears likely to exceed the cardiac NOAEL in normal streaming applications. Table 8 gives the global environmental characteristics.

One potential problem that occurs with many (but not all) **of** the new halocarbon agents is that they generate **4** to 10 times more hydrogen fluoride than halon 1301 does during comparable extinguishment. Although a large amount of information is available on hydrogen fluoride toxicity, it is difficult to determine what risk is acceptable. Moreover, insufficient data exist to determine what hydrogen fluoride levels are likely in real fire scenarios. In general, agent decomposition products and combustion products increase with fire size and extinguishment time. To minimize decomposition and combustion products, rapid detection and rapid discharges are recommended.

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*All percentage concentrations given in this paper are percent by volume.

TABLE 3. COMMERCIALIZED TOTAL-FLOODING HALON REPLACEMENTS.

Agent	Chemical	Formula	Trade Name
HCFC-124	Chlorotetrafluoroethane	$CHClFCF_3$	DuPont “E-241’’
HCFC Blend A HCFC-123 HCFC-22 HCFC-124	Additive plus Dichlorotrifluoroethane Chlorodifluoromethane Chlorotetrafluoroethane	 $CHCl_2CF_3$ $CHClF_2$ $CHClFCF_3$	North American Fire Guardian “NAF S-III”
HFC-23	Trifluoromethane	CHF_3	DuPont “E-13”
HFC-125	Pentafluoroethane	CHF_2CF_3	DuPont “FE-25”
HFC-227ea	Heptafluoropropane	CF_3CHFCF_3	Great Lakes “FM-200”
HFC-236fa	1,1,1,3,3,3-Hexafluoropropane	$CF_3CH_2CF_3$	DuPont “E-36”
FC-218	Perfluoropropane	$CF_3CF_2CF_3$	3M “CEA-308”
FC-3-1-10	Perfluorobutane	$CF_3CF_2CF_2CF_3$	3M Company “CEA 4 1 0
FIC-1311	Trifluoroiodomethane	CF_3I	Pacific Scientific “Triodide”; West Florida Ordnance “Iodoguard”; Ajay North America

Agent	Minimum Design Concentration for n-Heptane, %	NOAEL, %	LOAEL, %
Halon 1301	5	5	7.5
HCFC-124	8.5	1.0	2.5
HFC-23	16	30	>50
HFC-125	10.9	7.5	10.0
HFC-227ea	7	9.0	10.5
HFC-236fa	6.4	10.0	15.0
FC-218	8.8	30	40
FC-3-1-10	**6.0**	40	>40
FIC-1311	3.6	0.2	0.4

TABLE 5. ENVIRONMENTAL CHARACTERISTICS, TOTAL-FLOODING AGENTS.

Agent	ODP	GWP	Lifetime, yrs
Halon 1301	12	5,400	65
HCFC-124	0.03	470	6.1
HCFC Blend A	0.044	1,450	12
HCFC-123	0.014	90	1.4
HCFC-22	0.04	1,500	12.1
HCFC-124	0.03	470	6.1
HFC-23	0.0	11,700	264
HFC-125	0.0	2,800	32.6
HFC-227ea	0.0	2,900	36.5
HFC-236fa	0.0	6,300	209
FC-218	0.0	7,000	2,600
FC-3-1-10	0.0	7,000	2,600
FIC-13I1	0.0001	<1	<0.005

TABLE 6. COMMERCIALIZED HALON REPLACEMENT STREAMING.

Agent	Chemical	Formula	Trade Name
HCFC-123	Dichlorotrifluoroethane	$CHCl_2CF_3$	DuPont “FE-232”
HCFC-124	Chlorotetrafluoroethane	$CHClFCF_3$	DuPont “FE-241”
HCFC Blend B	Primarily		American Pacific “Halotron I”
HCFC-123	Dichlorotrifluoroethane	$CHCl_2CF_3$	
HCFC Blend C	Proprietary additive plus		North American Fire Guardian “NAF P-III”
HCFC-123	Dichlorotrifluoroethane	$CHCl_2CF_3$	
HCFC-124	Chlorotetrafluoroethane	$CHClFCF_3$	
HFC-134a	1,1,1,2-Tetrafluoroethane	CH_2FCF_3	
HCFC Blend D	Proprietary additive plus		North American Fire Guardian “BLITZ”
HCFC-123	Dichlorotrifluoroethane	$CHCl_2CF_3$	
HFC-227ea	Heptafluoropropane	CF_3CHFCF_3	Great Lakes “FM-200”
HFC-236fa	1,1,1,3,3,3-Hexafluoropropane	$CF_3CH_2CF_3$	DuPont “FE-36”
FC-5-1-14	Perfluorohexane	$CF_3(CF_2)_4CF_3$	3M Company “CEA 614”
FIC-13I1	Trifluoroiodomethane	CF_3I	Pacific Scientific “Triodide”; West Florida Ordnance “Iodoguard”

TABLE 7. TOXICITY PROPERTIES OF COMMERCIALIZED STREAMING AGENTS.

Agent		NOAEL, %	LOAEL. %
Halon 1211		0.5	1.0
HCFC-123		1.0	2.0
HCFC-124		1.0	2.5
HCFC Blend B:	HCFC-123	1.0	2.0
HCFC Blend C:	HCFC-123	1.0	2.0
	HCFC-124	1.0	2.5
	HFC-134a	4.0	8.0
HCFC Blend D:	HCFC-123	1.0	2.0
HFC-227ea		9.0	10.5
HFC-236fa		10.0	15.0
FC-5-1-14		40	>40
FIC-1311		0.2	0.4

TABLE 8. ENVIRONMENTAL CHARACTERISTICS, STREAMING AGENTS

Agent		ODP Relative to CFC-I1	GWP Relative to CO_2	Atmospheric Lifetime, yrs
Halon 1211		**5.1**		20
HCFC-123		0.014	90	1.4
HCFC-124		0.03	470	6.1
HCFC Blend B:	HCFC-123	0.014	90	1.4
HCFC Blend C:	HCFC-123	0.014	90	1.4
	HCFC-124	0.03	470	6.1
	HFC-134a	0.0	1300	14.6
HCFC Blend D:	HCFC-123	0.014	90	1.4
HFC-227ea		0.0	2900	36.5
HFC-236fa		0.0	6300	209
FC-5-1-14		0.0	7400	3200
FIC-13I1		0.0001	<1	<0.005

Commercialized Alternatives

Nonhalocarbon substitutes are increasingly being considered for replacement of halons. Already, water sprinklers are replacing halon systems in many applications. Dry chemical extinguishants and carbon dioxide are also receiving increased use. Alternatives can be divided into two types: "Classical" Alternatives and "New" Alternatives (Table 9). Note that the word "New" does *not* necessarily imply that the technology was developed recently, but that there is a new **or** renewed interest in the use of the technology as a replacement for halons. The following presents some discussions of only "New" Alternatives.

TABLE 9. ALTERNATIVES.

Classical	New
Foams	Water Misting
Water Sprinklers	Particulate Aerosols
Dry Chemicals	Inert Gases
Carbon Dioxide	Gas Generators
Loaded Stream	Combination

Water Misting

Water misting systems allow the use of fine water sprays to provide fire protection with reduced water requirements and reduced secondary damage. Calculations indicate that on a weight basis, water could provide fire extinguishment capabilities better than those of halons, provided that complete or near-complete evaporation of water is achieved. Since small droplets evaporate significantly faster than large droplets, the small droplets achievable through misting systems could approach this capability. The **NFTA** 750 Standard on water misting systems [4] establishes 1000 microns (micrometers, μm) or less as being the water droplet size for a system to be designated as a water misting system; however, many misting systems have droplet sizes well below this value. The NFPA 750 Standard defines three classes of water mists from finer to coarser based on the size distribution of the water droplets produced. As an approximate definition, the droplet sizes are less than 200 microns for a Class 1 Mist (the finest), 200 to 400 microns for a Class **2** Mist, and 400 **to** 1000 microns for a Class 3 Mist (the coarsest). The actual definitions are more complex and are based on the size distribution curve.

There are two basic types of water mist suppression systems — single-fluid and twin-fluid. Single-fluid systems utilize water stored or pumped under pressure; twin-fluid systems use air, nitrogen, or another gas to atomize water at a nozzle. The systems can also be classified according *to* the pressure on the distribution system piping as high-pressure (above 500 psia [34.5 bar]), intermediate-pressure (175 to 500 psia [12.1 to 34.5 bar]), and low-pressure (175 psia [12 bar] **or** less). Both single-fluid and twin-fluid systems have been shown to be promising fire suppression systems. Single-fluid systems have lower space and weight requirements, reduced piping requirements, and easier system design and installation; twin-fluid systems require lower water supply pressure, larger nozzle orifices (greater tolerance to dirt and contaminants and may allow the use of higher viscosity antifreeze mixtures), and increased control **of** drop size.

Table 10 gives a list of manufacturers for water misting systems. Since the manufacturers of these systems are constantly changing and the number is continuously increasing, this list will necessarily be incomplete.

TABLE 10. COMMERCIAL AND NEAR-COMMERCIAL MISTING SYSTEMS.

Twin-Fluid	Single-Fluid
ADA Technologies, USA	Baumac International MicroMist
GEC-Marconi Avionics, UK	FOGTEC, Germany
Ginge-Kerr, U.K., Denmark, Norway	Grinnell AquaMist, USA
Kidde International, UK, USA	GW Sprinkler, Denmark
Secuirplex Firescope 2000, Canada	KAMAT, Germany
	Kidde International, UK, USA
Technology Unknown	Marioff Oy Hi-fog, Finland
DAR CHEM, UK	Phirex, U.K./Sprinklerhuest, Sweden
HTC, Sweden	Semco Marine, USA/Denmark
	Spraying Systems, USA
	Total Walther/Wormald MicroDrop
	Unifog Water Mist, Germany
	Unitor, Germany

Particulate Aerosols

A number of fire extinguishing products have been announced as producing very finely divided dry chemical suspensions (particulate aerosols). In many, if not all cases, the aerosol is **a** potassium salt suspension produced by combustion and is termed a “pyrotechnically generated aerosol” (PGA). Among the companies now marketing particulate aerosol technologies are Spectronics in Israel and Spectrex in the U.S. (“S.F.E.” agents), Pyrogen Corporation in Australia (“PyroGen”), and Dynamit Nobel in Germany (“Soyus” extinguishers).

Inert Gases

Combustion cannot occur when the oxygen content of air at normal pressures is sufficiently reduced (below approximately 15%, fires cannot be initiated; at lower concentrations, fires are extinguished). Thus, inert gases such as nitrogen, argon, etc., can extinguish fires by diluting the air and decreasing oxygen content. Extinguishment is also facilitated by heat absorption.

A number of pure **and** blended inert gases are being marketed as alternatives to halons (Table 11). The concentrations needed **for** extinguishment are approximately 34 to 52%, depending on the fuel and the fire scenario. The extinguishing properties of argon are similar to those of nitrogen **for** Class A, B, and C fires; however, unlike nitrogen, argon is suitable for Class D fires involving metals that react with nitrogen (e.g., magnesium and lithium).

TABLE 11. INERT GASES.

Designation	Composition	Manufacturer
IG-541	Nitrogen 52% ± 4% Argon 40% ± 4% CO_2 8% ± 1	Tyco International, Ltd., USA, and Fire Eater A/S, Denmark ("INERGEN")
IG-55	Nitrogen 50% ± 5 Argon 50% ± 5	Ginge-Kerr Denmark A/S ("ARGONITE")
IG-01	100% Argon	Minimax GmbH ("Argotec")
IG-1	100% Nitrogen	Cerberus AG, Germany; Koatsu ("NN100"), Japan

The US EPA allows inert gas design concentrations to an oxygen level of 10% (52% agent) if egress can occur within 1 min, but to an oxygen level of no lower than 12% (43% agent) if egress requires more than 1 min. Designs to oxygen levels of less than 10% are allowed only in normally unoccupied areas and only if personnel who could possibly be exposed can egress in less than 30 sec.

In place of cardiac sensitization NOAEL and LOAEL values, which are inappropriate for inert gases, the 1996 NFPA 2001 Standard [1] uses a No Effect Level (NEL) and a Low Effect Level (LEL). These values are based on physiological effects in humans in hypoxic atmospheres and are the functional equivalents of the NOAEL and LOAEL values given for halocarbons. All inert gas agents listed in the 1996 Standard (IG-01, IG-541, and IG-55) have sea-level-equivalent NEL and LEL values of 43% (12% oxygen) and 52% (10% oxygen), respectively. Similar to that done for halocarbon agents, the Standard allows the use of an inert gas agent up to the LEL value for Class B hazards in normally occupied areas where a predischarge alarm and time delay are provided. In the absence of a time delay, only design concentrations up to the NEL are allowed. A major difference between NFPA and US EPA approaches is that the US EPA bases allowable design concentrations on specific egress times.

NEAG/HAG recommends that oxygen concentrations in occupied areas protected by inert gas systems not be less than 12% unless a room can be evacuated in 1 min (2 min in the case of "INERGEN). This oxygen level corresponds to an inert gas concentration of 43%. NEAG/HAG also recommends that exposures to oxygen levels less than 10% not be allowed for any period of time.

Gas *Generators*

Gas generator technology utilizes ignition of solid propellants to generate large quantities of gases. This gaseous effluent can be either used as is to create an inert environment or enhanced with various active agents to more aggressively attack the fire. This technology is new, and much of it is still in the research and development stage. Olin Aerospace Company, which has been supporting U. S. Department of Defense (DoD) testing, has announced that initial engineering, manufacturing, and development contracts have been received from two airframe manufacturers to protect aircraft dry bay. Primex Aerospace markets FS 0140 for use as a total-flooding agent in unoccupied areas. Walter Kidde Aerospace has teamed with Atlantic Research Corporation to develop gas generator technology for aviation and defense applications.

Combination

Mixtures with water or with halocarbon bases have been marketed for many years. One example is the "loaded stream" type of agents that have been used in the past. In addition, blends of dry chemicals with halons or other halocarbons, sometimes with a gelling agent, have been marketed. With the phaseout of halons, there is increased interest in and development of such mixtures. Among the commercial products are (1) "Envirogel," a series of blends containing one or more halocarbons, a dry chemical, and a gelling agent, produced by POWSUS, Inc., in the US, *(2)* ColdFire *302,* a mixture of organic surfactants and water, manufactured by North American Environmental Oil & Chemical Cleaning Supply Co., and *(3)* Fire-X-Plus, a foam produced by Firefox Industries in the US. There are, undoubtedly, many other combination agent products being commercialized or being developed for commercialization.

Summary

Many commercialized options to the use of halons are now available, but tradeoffs are needed in most applications. Due to the multiple choices available and required tradeoffs, careful fire protection engineering is required to select and employ the best option for each application.

References

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