

**MONTREAL PROTOCOL
ON SUBSTANCES THAT DEplete
THE OZONE LAYER**



UNEP

**REPORT OF THE
HALONS TECHNICAL OPTIONS COMMITTEE
DECEMBER 2014**

**TECHNICAL NOTE #1 – REVISION 4
FIRE PROTECTION ALTERNATIVES TO HALONS**

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Fire Protection Alternatives To Halon

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Preface

Technical Note #1, *Fire Protection Alternatives to Halons*, replaces the chapters on this subject that have been part of previous Assessment Reports of the UNEP Halon Technical Options Committee (HTOC). Future reports, including the 2014 Assessment Report, will contain an abbreviated chapter that briefly introduces the subject of *Alternatives* and refers the interested reader to this document. The HTOC elected to take this approach as much of the information that, while important to understand when developing strategies for selecting alternatives to halons, has been largely reported in prior editions of Assessment Reports. The Assessment Reports contain important new updates on evolving technologies but this usually forms only a small portion of the chapter content. As such, it was deemed by the HTOC to make the *Alternatives* subject a stand-alone document that is referenced by future Assessment Reports. By this approach those having particular interest in the technical aspects of the *Alternatives* subject can access a self-contained document addressing those issues.

1.0 Introduction

1.1 Overview

Technical Note #1 addresses the technical aspects of the alternatives available to the use of halons, ozone depleting substances (ODS), as fire extinguishing agents. As such, it is useful to understand the different types of fires as they relate to selection of the best available alternatives to halon extinguishing agents.

There are several categories of fire types based on the physical or chemical nature of the fuel involved. The designation of the classification of fuel types varies by region and is summarised below.

Table 1: Classifications of fuel types by region

Region	Fuel Type Classification		
	United States	Europe	Australia & Asia
Ordinary combustibles (wood, paper, plastics, etc.)	Class A	Class A	Class A
Flammable liquids	Class B	Class B	Class B
Flammable gases	Class B	Class C	Class C
Electrical equipment	Class C	n/a	Class E
Combustible metals	Class D	Class D	Class D
Cooking oil or fat	Class K	Class F	Class F

Halons were not used on fires involving combustible metals. Nor were they used for fire extinguishment in commercial cooking applications (hot cooking oils). Halons were commonly used for fire protection in applications involving the other listed fire classes - ordinary combustibles, flammable liquids, flammable gases, and electrical equipment. Each fire protection

application involving one or more of these fire types has distinct characteristics that must be considered in selecting the best halon-alternative fire protection technology. Examples of important application characteristics include: temperature, pressure, and altitude above sea level of the protected space; temperature of the location of the agent storage tanks; whether or not the space may be occupied at the time a fire occurs; whether fire extinguishing is to be achieved by local application of an agent directly onto burning materials or by creation of a fire extinguishing atmosphere in a defined volume (total flooding); pressure strength of the enclosure; availability of a water supply; asset value of objects and spaces being protected; ability to minimize collateral damage and thereby limit downtime of equipment; sensitivity of protected objects and spaces to collateral damage by water or combustion gases (including agent decomposition gases, if applicable) .

Halons, as defined in Group II of Annex A of the Montreal Protocol (MP), form a class of halogenated chemicals containing bromine that have been and continue to be used as gaseous extinguishing agents in a wide range of fire and explosion protection applications. Halons are very potent stratospheric ozone depleting chemicals when released to the atmosphere. Halons have been phased out of production under the MP. The phase-out of halon production has had a dramatic impact on the fire and explosion protection industry. Halons are clean, non-conductive, and highly effective. Halon 1301, in particular, is safe for people when used at concentrations typically employed for “total flooding” fire extinguishing systems and explosion prevention (inerting) applications. Halon 1211 was widely employed as a “streaming agent” in portable fire extinguishing units. Halon 2402 has been used in both total flooding and streaming agent applications. Fire extinguishing agent alternatives to halons, in the form of non-ozone depleting gases, gas-powder blends, powders, and other not-in-kind technologies (i.e., non-gaseous agents) are now available for the majority of fire and explosion protection application once served by halons.

Selection of the best fire protection method in the absence of halons is often a complex process. Either alternative gaseous fire extinguishing agents, or other agent types or extinguishing methods, may be used in place of halon, but the decision is driven by the details of the hazard being protected, the characteristics of the gaseous agent or alternative method, and the risk management philosophy of the user.

Gaseous extinguishing agents that are electrically non-conductive and which leave no residue are referred to as “clean” agents. (Owing to its toxicity, carbon dioxide is not a useful alternative to halon 1301 when exposure of personnel to the agent vapor is a safety consideration.) Several clean agents and new “not-in-kind” alternative technologies have been introduced to the market. The purpose of this technical note is to provide a brief review of the types of alternatives to halons that are available, including information on physical and chemical characteristics, fire protection capabilities and toxicity, and key environmental parameters.

Since the 2010 Assessment, there have been some changes made to national and international fire protection standards, namely NFPA 2001 and ISO-14520, that affect some of the measures of performance and guidelines for use of the agents described herein.

- NFPA 2001 now recognizes that that Class A fire hazards involving electrified equipment may pose additional extinguishing risks. In such cases higher minimum agent design concentrations are recommended.
- Both NFPA 2001 and ISO-14520 are now in harmony with respect to requiring a 30 % minimum safety factor where the fire hazard is due to Class B flammable and combustible liquids. The minimum safety factor for Class A surface fire hazards is either 20 % or 30 %, depending on the governing standard and the type of agent. This means that the minimum design concentration (MDC) of a gaseous fire extinguishing agent must be at least 1.2 or 1.3 times the minimum extinguishing concentration (MEC), as determined by test, for a particular fire hazard and depending on which standard governs the application.

The following two subsections provide an overview of toxicity and environmental aspects of alternatives to halons. More detailed information on these topics and other agent properties is presented in sections 2.0 and 3.0, which address total flooding and streaming agents, respectively.

1.2 Agent Toxicity

In general, personnel should not be exposed unnecessarily to atmospheres into which gaseous fire extinguishing agents have been discharged. Mixtures of air and halon 1301 have low toxicity at fire extinguishing concentrations and there is little risk posed to personnel that might be exposed in the event of an unexpected discharge of agent into an occupied space. The acceptance of new agents for use in total flooding fire protection in normally occupied spaces has been based on criteria that have evolved over the period of introduction of new technologies into the marketplace. In the case of inert gas agents the usual concern is the residual oxygen concentration in the protected space after discharge. For chemical agents the primary health issue is cardiac effects as a consequence of absorption of the agent into the blood stream. The highest agent concentration for which no adverse effect is observed is designated the “NOAEL” for “no observed adverse effect level”. The lowest agent concentration for which an adverse effect is observed is designated the “LOAEL” for “lowest observed adverse effect level”. This means of assessing chemical agents has been further enhanced by application of physiologically based pharmacokinetic modelling, or “PBPK” modelling, which accounts for exposure times. Some agents have their use concentration limits based on PBPK analysis. The approach is described in more detail in ISO 14520-1, Annex G, 2nd Edition (2006). Health issues for the other alternatives (e.g. CO₂, water mist, fine solid particulate) are described in more detail later in this document.

1.3 Environmental Factors

The primary environmental factors to be considered for halocarbon agents¹ are ozone-depletion potential (ODP), global-warming potential (GWP), and atmospheric lifetime, values of which are noted in Tables 1-2, 1-3, 1-6, 1-13, 1-17, 1-18, 1-19, and 1-27. It is important to select the fire

¹ Halocarbon agents are halogenated hydrocarbon chemicals, including hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), a fluoroketone (FK), and a fluoroiodocarbon (FIC), that are used for fire-fighting applications. Each of these chemicals is stored either as a liquefied compressed gas or as a liquid at room temperature, is electrically non-conductive, and leaves no residue upon vapourisation..

protection choice with the lowest environmental impact that will provide the necessary fire protection performance for the specific application. The use of any synthetic compound that accumulates in the atmosphere carries some potential risk with regard to atmospheric equilibrium changes. Perfluorocarbons (PFCs), in particular, represent an unusually severe potential environmental impact due to the combination of extremely long atmospheric lifetime and high GWP. PFCs are no longer used as primary extinguishants in new systems, though a small amount of CF₄, less than 2 %, is used as an additive in HCFC-Blend B, a streaming agent. PFC use in legacy systems is diminishing. Thus, PFC agents are not considered to be viable alternatives to halons and are not addressed further. International agreements and individual actions by national governments may affect future availability of several compounds and subsequent support for installed fire protection systems that utilise them. Some examples are presented below:

- HCFCs are scheduled for a production and consumption² phase out for fire protection uses under the Montreal Protocol in 2020 in non-Article 5 Parties and 2030 in Article 5 Parties.
- The United Nations Framework Convention on Climate Change (UNFCCC) has identified carbon dioxide, methane, nitrous oxide and the fluorochemicals HFCs, PFCs and SF₆ as the basket of long-lived (>1 year) gases primarily responsible for anthropogenic changes to the greenhouse effect and potentially subject to emission controls. All uses of fluorochemicals represent 4–5% of current worldwide greenhouse gas emissions from long-lived gases on a carbon equivalent basis and fire protection uses represent less than 1% of those fluorochemical emissions.
- In the EU, Regulation (EU) No. 517/2014 (known as the F Gas Regulation), establishes rules on containment, use, recovery and destruction of fluorinated greenhouse gases in order to protect the environment. Related ancillary measures impose conditions on the placing on the market of specific products and equipment that contain, or whose functioning relies upon, fluorinated greenhouse gases, and establishes quantitative limits for the placing on the market of hydrofluorocarbons.

2.0 Total Flooding Agents

A number of fire extinguishing agent technologies have been commercialised as alternatives to halons for use in total flooding applications. Attributes of these are summarised in the subsections below.

Several agents have been incorporated into consensus standards, specifically NFPA 2001, ISO-14520 and other national standards, for use in normally occupied spaces. These agents include certain inert gases, hydrofluorocarbons (HFCs), a fluoroketone (FK), and a fluoroiodocarbon (FIC). These agents may be used for total flooding fire protection in normally occupied spaces provided that the design concentration is below the safe exposure threshold limits shown in Tables 2, 3, 5, and 9.

The United States Environmental Protection Agency (EPA), under the Significant New Alternatives Policy (SNAP) program, has reviewed a number of materials as substitutes for

² Consumption equals production plus imports minus exports for an individual country.

halons as fire extinguishing agents. The approval status in the United States of a number of such alternatives for use in total flooding systems may be found at the EPA website.³

Agencies of other countries administer their own regulations on suitability of alternatives to halons. One example is in Germany, the Berufsgenossenschaftliche. There is no European wide or other regional regulations on alternatives to halons.

2.1 Halocarbon agents

The tables below summarize key attributes of commercially available, technically proven halocarbon alternatives to halons for total flooding fire protection using fixed systems. The attributes addressed relate to efficacy, toxicity, volatility, environmental and relative cost characteristics. Cost effectiveness is represented by an index that is benchmarked against carbon dioxide total flooding systems, averaged over a wide range of application sizes, exclusive of the cost of pipe, fittings and installation and is based on 2003 data. Owing to commercial confidentiality, it has not been possible to use more current data, but nevertheless the indices are believed to be relatively accurate.

³ See U.S. EPA, SNAP Program

Table 2: Non-ODS Halocarbon Agents

Agent	FK-5-1-12	HFC-23	HFC-125	HFC-227ea
Efficacy	For use in occupied spaces MDC(A) = 5.3 vol% MDC(B) = 5.9 vol% (1)	For use in occupied spaces MDC(A) = 16.3 vol% MDC(B) = 16.4 vol% • Suitable for inerting some flammable atmospheres at concentrations below the LOAEL value. • Suitable for use at low temperatures (below -20 °C).	For use in occupied spaces MDC(A) = 11.2 vol% MDC(B) = 12.1 vol%	For use in occupied spaces MDC(A) = 7.9 vol% MDC(B) = 9.0 vol%
Toxicity	NOAEL = 10 vol% LOAEL > 10 vol%	NOAEL = 30 vol% LOAEL > 30 vol%	NOAEL = 7.5 vol% LOAEL = 10 vol% Approved for use in occupied spaces at up to 11.5 vol% based on PBPK modelling.	NOAEL = 9 vol% LOAEL = 10.5 vol% Approved for use in occupied spaces at up to 10.5 vol% based on PBPK modelling.
Some acidic decomposition products are formed when a halogenated fire extinguishing agent extinguishes a fire.				
Safety Characteristics	Liquid at 20 °C B.P. = 49.2 °C	Liquefied compressed gas. B.P. = -82 °C	Liquefied compressed gas. B.P. = -48.1 °C	Liquefied compressed gas. B.P. = -16.4°C
Environmental Characteristics (2)	ODP = 0 GWP = <1	ODP = 0 GWP = 12 400	ODP = 0 GWP = 3170	ODP = 0 GWP = 3350
Cost-Effectiveness, avg. for 500 to 5000 m3 volume (2003 data)	~1.7 to 2.0	~2.0 to 2.3	Not available	~1.5

Note 1: MDC(A) and MDC(B) refer to the minimum design concentration for a Class A or Class B fire hazard.

Note 2: Source: IPCC 5th WGI Assessment Report

The agents addressed in Table 3 are ozone depleting substances. While use of these agents is permitted for use in new fire extinguishing systems in many jurisdictions, the practice at present is primarily to use these agents to recharge legacy systems and to choose non-ozone-depleting agent for new systems.

Table 3: HCFC Halocarbon Agents

Agent	HCFC Blend A 82 wt% HCFC 22 9.5 wt% HCFC 124 4.75 wt% HCFC 123 3.75 wt% isopropenyl-1-methylcyclohexane	HCFC-124												
Efficacy	For use in occupied spaces MDC(A) = 7.9 vol% MDC(B) = 9.0 vol%	For use in unoccupied spaces MDC(A) = (1) MDC(B) = 8.7 vol%												
Toxicity	NOAEL = 10 vol% LOAEL > 10 vol%	NOAEL = 1 vol% LOAEL = 2.5 vol%												
	Some acidic decomposition products are formed when a halogenated fire extinguishing agent extinguishes a fire.													
Safety Characteristics	B.P. = -38.2 °C	B.P. = -12.1 °C												
Environmental Characteristics (2)	<table border="1"> <thead> <tr> <th></th> <th>ODP</th> <th>GWP</th> </tr> </thead> <tbody> <tr> <td>HCFC-22</td> <td>0.055</td> <td>1,760</td> </tr> <tr> <td>HCFC 124</td> <td>0.022</td> <td>527</td> </tr> <tr> <td>HCFC-123</td> <td>0.02</td> <td>79</td> </tr> </tbody> </table>		ODP	GWP	HCFC-22	0.055	1,760	HCFC 124	0.022	527	HCFC-123	0.02	79	ODP = 0.022 GWP = 527
	ODP	GWP												
HCFC-22	0.055	1,760												
HCFC 124	0.022	527												
HCFC-123	0.02	79												
Cost-Effectiveness, avg. for 500 to 5000 m3 volume (2003 data)	Varies from 1 to 2	Varies from 1 to 2												

Note 1: Not reported

Note 2: Source: IPCC 5th WGI Assessment Report

The table below summarizes key physical properties of halocarbon agents including vapour pressure, vapour density, and liquid density at 20 °C, and the constants k_1 and k_2 that are used to calculate agent vapour specific volume (s) as a function of temperature at one-atmosphere pressure (1.013 bar) using the following equation: $s = k_1 + k_2 \cdot t$ where t is in °C and s has the units kg/m^3 .

Table 4: Physical Properties (20 °C) of Halocarbon Agents Used in Total Flooding Applications (1)

Generic Name	Vapour Pressure (bar)	Liquid Density (kg/m^3)	k_1 (m^3/kg) (2)	k_2 ($\text{m}^3/\text{kg}\cdot^\circ\text{C}$) (2)	s, Vapour Specific Volume (m^3/kg)	Vapour Density (kg/m^3)
Halon 1301 (a)	14.3	1,574	0.14781	0.000567	0.1592	6.283
HCFC Blend A	8.25	1,200	0.2413	0.00088	0.2589	3.862
HFC-23	41.8	807	0.3164	0.0012	0.3404	2.938
HFC-125	12.05	1,218	0.1825	0.0007	0.1965	5.089
HFC-227ea	3.9	1,41	0.1269	0.000513	0.1372	7.29
HFC-236fa	2.3	1,377	0.1413	0.0006	0.1533	6.523
FK-5-1-12	0.33	1,616	0.0664	0.000274	0.0719	13.912
HFC Blend B (b)	12.57	1,190	0.2172	0.0009	0.2352	4.252

Note 1: All values from ISO 14520 except where noted: (a) NFPA 12A (2009) and Thermodynamic Properties of Freon 13B1 (DuPont T-13B1); (b) American Pacific Corp.

Note 2: Agent vapour specific volume is calculated as $s = k_1 + k_2 \cdot t$ at standard atmospheric pressure, 1.013 bar, where t is the vapour temperature in °C. Vapour density = $1/s$.

The table below summarizes for halocarbon agents the minimum extinguishing concentrations for Class A and Class B fires, as determined by standardised tests, the minimum inerting concentration to prevent flame propagation in a mixture of methane and air, and the NOAEL and LOAEL toxicity limits.

Table 5: Halocarbon Agents Used in Total Flooding Applications – Minimum Extinguishing Concentrations and Agent Exposure Limits

Generic Name ISO 14520 reference	Minimum Design Conc., Class A Fire vol % (1)	Minimum Design Conc., Class B Fire vol % (1)	Inerting Conc. Methane /Air, vol %	NOAEL vol % (2)	LOAEL vol % (2)	Maximum Conc. for 5 min. Exposure, vol % (6)
Halon 1301	5.0 (3)	5.0 (3)	4.9	5	7.5	-
HCFC Blend A ISO 14520-6	13.0 (7)	13.0	20.5	10	>10	10
HFC-23 ISO 14520-10	16.3	16.4	22.2	30	>50	30
HFC-125 ISO 14520-8	11.2	12.1	-	7.5	10	11.5
HFC-227ea ISO 14520-9	7.9	9.0	8.8	9	10.5	10.5
HFC-236fa ISO 14520-11	8.8	9.8	-	10	15	12
FK-5-1-12 ISO 14520-5	5.3	5.9	8.8	10	>10	10
HFC Blend B (4)	14.7 (5)	14.7	-	5	7.5	5

Note 1: Minimum design concentration as given in Table 5 of ISO 14520-(agent-specific volume), where available.

Note 2: A halocarbon agent may be used at a concentration up to its NOAEL value in normally occupied enclosures provided the maximum expected exposure time of personnel is not more than five minutes. A halocarbon agent may be used at a concentration up to the LOAEL value in normally occupied and normally unoccupied enclosures provided certain criteria are met that depend on agent toxicity and egress time. The reader is referred to NFPA 2001-1.5 (2008) and ISO 14520-G.4.3 (2006) for details of the recommended safe exposure guidelines for halocarbon agents.

Note 3: Exceptions, halon 1301 design concentration is taken as the historical employed value of 5%.

Note 4: Not approved for use in occupied spaces.

Note 5: Agent manufacturer did not provide Class A extinguishing concentration data. Class A design concentration in this case was taken as Class B design concentration.

Note 6: Agent exposure guidance is as indicated in ISO 14520-1 (2006) Annex G.

The table below summarizes the environmental attributes of halocarbon agents including ozone depletion potential (ODP), 100-year global warming potential (GWP), and atmospheric lifetime.

Table 6: Halocarbon Agents Used in Total Flooding Applications – Environmental Factors

Generic Name	Ozone Depletion Potential (1)	Global Warming Potential, 100 yr. (2)	Atmospheric Life Time, yr. (2)
Halon 1301	10	7,140	65
HCFC-22 (component in HCFC Blend A)	0.055	1,760	11.9
HCFC-124 (component in HCFC Blend A)	0.022	527	5.9
HCFC-123 (component in HCFC Blend A)	0.02	79	1.3
HFC-23	0	12,400	222
HFC-125	0	3,170	28.2
HFC-227ea	0	3,350	38.9
HFC-236fa	0	8,060	242
FK-5-1-12	0	< 1	7 days
HFC-134a (component in HFC Blend B)	0	1,300	13.4
HFC-125 (component in HFC Blend B)	0	3,170	28.2

Note 1: Source: Montreal Protocol Handbook (2012)

Note 2: Source: IPCC 5th WGI Assessment Report

The table below summarizes information relating relative agent efficacy for Class A total flooding fire protection applications including agent quantities per unit volume of protected space, typical cylinder fill densities, cylinder storage volume relative to halon 1301, and typical cylinder charging pressures.

Table 7: Halocarbon Agents Used in Total Flooding Applications – Agent Quantity Requirements (20 °C) for Class A Combustible Hazard Applications (1, 2)

Generic Name	Agent Mass, kg/m ³ of Protected Volume	Mass Relative to Halon 1301	Agent Liquid Volume litre/m ³ of Protected Volume	Maximum Cylinder Fill Density, kg/m ³ (3)	Cylinder Storage Volume Relative to Halon 1301 (4)	Cylinder Pressure @ 20°C, bar
Halon 1301 (5)	0.331	1.000	0.210	1,121	1.00	25 or 42
HCFC Blend A	0.577	1.74	0.481	900	2.17	25 or 42
HFC-23	0.572	1.73	0.708	860	2.25	43
HFC-125	0.701	1.93	0.525	929	2.33	25
HFC-227ea	0.722	1.89	0.444	1,150	1.84	25 or 42
HFC-236fa	0.629	1.91	0.459	1,200	1.78	25 or 42
FK-5-1-12	0.779	2.35	0.482	1,480	1.78	25, 34.5, 42 or 50
HFC Blend B (6,7)	0.733	2.22	0.616	929	2.67	25 or 42

Note 1: Halon alternative agent quantities based on a safety factor of 1.3. Nominal maximum discharge time is 10 seconds in all cases.

Note 2: Mass and volume ratios based on Minimum Class A Fire Design Concentrations. See Table 5.

Note 3: Fill density based on 25 bar pressurisation except for HFC-23.

Note 4: Agent cylinder volume per m³ protected volume = (Agent Mass, kg/m³ protected volume) / (Maximum Fill Density, kg/m³ cylinder) = (V_{CYL}/V_{ProtVol}). For halon 1301 cylinder volume per m³ hazard = (0.331 kg/m³ hazard) / (1,121 kg/m³ cylinder) = 0.0002953 m³ cylinder / m³ protected volume.

Note 5: NFPA 12A; ASTM D5632.

Note 6: Agent manufacturer did not supply complete Class A extinguishing data, hence no Class A MDC established; the heptane MDC was employed in this table.

Note 7: NFPA 2001 (2012).

The table below summarizes information relating relative agent efficacy for Class B total flooding fire protection applications including agent quantities per unit volume of protected space, typical cylinder fill densities, cylinder storage volume relative to halon 1301, and typical cylinder charging pressures.

Table 8: Halocarbon Agents Used in Total Flooding Applications - Agent Requirements for Class B Fuel Applications (1, 2)

Generic Name	Agent Mass, kg/m ³ of Protected Volume	Mass Relative to Halon 1301	Agent Liquid Volume litre/m ³ of Protected Volume	Maximum Cylinder Fill Density, kg/m ³ (3)	Cylinder Storage Volume Relative to Halon 1301 (4)	Cylinder Pressure @ 20°C, bar
Halon 1301	0.331	1.00	0.210	1,121	1.00	25 or 42
HCFC Blend A	0.577	1.74	0.481	900	2.17	25 or 42
HFC-23	0.575	1.74	0.713	860	2.27	43
HFC-125	0.698	2.11	0.573	929	2.55	25
HFC-227ea	0.720	2.18	0.512	1,150	2.12	25 or 42
HFC-236fa	0.711	2.15	0.516	1,200	2.01	25 or 42
FK-5-1-12	0.872	2.63	0.540	1,480	2.00	25, 34.5, 42 or 50
HFC Blend B	0.733	2.22	0.616	929	2.67	25 or 42

Note 1: Halon alternative agent quantities based on a safety factor of 1.3. Nominal maximum discharge time is 10 seconds in all cases.

Note 2: Mass and volume ratios based on "Minimum Class B Fire Design Concentrations." See Table 5.

Note 3: Fill density based on 25 bar pressurisation except for HFC-23.

Note 4: Agent cylinder volume per m³ of protected volume = (Agent Mass, kg/m³ of protected volume)/(Maximum Fill Density, kg/m³ cylinder) = (V_{CYL}/V_{ProtVol}). For halon 1301 cylinder volume per m³ of protected volume = (0.331 kg/m³ hazard)/(1,121 kg/m³ cylinder) = 0.0002953 m³ cylinder/m³ of protected volume.

2.2 Inert Gas Clean Agents

Inert gas clean agents have zero ODP and zero GWP.⁴ There have been at least four inert gases or gas mixtures commercialised as clean total flooding fire suppression agents. Inert gas agents are typically used at design concentrations of 35 vol % to 50 vol %, which reduces the ambient oxygen concentration to between 14 vol % to 10 vol %, respectively. Reduced oxygen concentration (hypoxia) is the principal human safety risk for inert gases except for carbon dioxide which has serious human health effects at progressive severity as its concentration increases above 4 vol %. Inert gas agents mixed with air lead to flame extinguishment by physical mechanisms only. The inert gas agents commercialised since 1990 consist of nitrogen,

⁴ Inert gas agent IG-541 contains 8 vol % carbon dioxide.

argon, and blends of nitrogen and argon. One blend contains 8 % carbon dioxide. The features of the commercialised inert gas agents are summarised in Tables 9 and 10.

These agents are electrically non-conductive, clean fire suppressants. The inert gas agents containing nitrogen or argon differ from halocarbon agents in the following ways:

- Inert gases can be supplied from high pressure cylinders, from low pressure cryogenic cylinders, or from pyrotechnic solids. High pressure systems use pressure reducing devices at or near the discharge manifold. This reduces the pipe thickness requirements and alleviates concerns regarding high pressure discharges.
- High pressure system discharge times are on the order of one to two minutes. This may limit some applications involving very rapidly developing fires.
- Inert gas agents are not subject to thermal decomposition and hence form no hazardous by-products.

The table below summarizes key attributes of inert gas clean agents.

Table 9: Inert Gas Clean Agents

Agent	IG-01	IG-100	IG-55	IG-541
Efficacy	For use in occupied spaces MDC(A) = 41.9 vol% MDC(B) = 51 vol %	For use in occupied spaces MDC(A) = 40.3 vol% MDC(B) = 43.7 vol %	For use in occupied spaces MDC(A) = 40.3 vol% MDC(B) = 47.5 vol %	For use in occupied spaces MDC(A) = 39.9 vol% MDC(B) = 41.2 vol %
Toxicity	Discharge of an inert gas system results in a significant reduction in the oxygen concentration within the protected area. See Table 11 regarding concentration and exposure limits for inert gas systems in normally occupied areas.			
Safety Characteristics	High-pressure compressed gas up to 300 bar			
Environmental Characteristics	No adverse characteristics			
Cost-Effectiveness, avg. for 500 to 5000 m3 volume (2003 data)	~1.8	~1.8	~1.8	~1.8

The table below summarises the main characteristics of inert gas agents including composition, environmental factors, physical properties, and minimum extinguishing concentrations for Class A and Class B fires.

Table 10: Properties of Inert Gas Agents for Fixed Systems

	IG-541 ISO 14520-15	IG-55 ISO 14520-14	IG-01 ISO 14520-12	IG-100 ISO 14520- 13
Generic name				
Agent composition				
Nitrogen	52 %	50 %		100 %
Argon	40 %	50 %	100 %	
Carbon Dioxide	8 %			
Environmental factors				
Ozone depletion potential	0	0	0	0
Global warming potential, 100 yr.	0	0	0	0
Physical properties				
k_1 , m ³ /kg (1)	0.65799	0.6598	0.5612	0.7998
k_2 , m ³ /kg-°C (1)	0.00239	0.00242	0.00205	0.00293
Specific Volume, m ³ /kg	0.697	0.708	0.602	0.858
Gas Density, 20 °C, 1 atm, kg/m ³	1.434	1.412	1.661	1.165
Extinguishing (2)				
Min. Class A fire design conc., vol %	39.9	40.3	41.9	40.3
Oxygen conc. at min. Class A design conc., vol %	12.6	12.5	12.2	12.5
Min. Class B fire design conc., vol %	41.2	47.5	51	43.7
Oxygen conc. at min. Class B design conc., vol %	12.3	11.0	10.3	11.8
Inerting design conc., Methane/Air, vol %	47.3	-	61.4	-
Oxygen conc. at min. inerting design conc., vol %	11.0	-	8.1	-

Note 1: Agent vapour specific volume = $k_1 + k_2 \cdot t$, m³/kg at an atmospheric pressure of 1.013 bar where t is the vapour temperature in °C. Vapour density = 1/s.

Note 2: Extinguishing and design concentration values from ISO 14520 2nd Edition (2006).

Physiological effects of inert gas agents

The primary health concern relative to the use of the inert gas agents containing nitrogen or argon is the effect of reduced oxygen concentration on the occupants of a space. The use of reduced oxygen environments has been extensively researched and studied. Many countries have granted health and safety approval for use of inert gases in occupied areas in the workplace. One product contains 8 vol % carbon dioxide⁵, which is included to increase blood oxygenation and cerebral blood flow in low-oxygen (hypoxic) atmospheres.

The table below contains exposure guidelines for non-liquefied inert gas agents that are described in detail in ISO 14520-1 (2006), Annex G.

Table 11: Exposure limits for inert gas agents

Inert Gas Concentration	Concentration Residual Oxygen Concentration	Permitted Occupancy	Exposure Time Limit
< 43 vol %	> 12 vol %	Normally occupied	5 min
43 to 52 vol %	10 to 12 vol %	Normally occupied	3 min
52 to 62 vol %	8 to 10 vol %	Normally occupied	30 sec
> 62 vol %	< 8 vol %	Normally unoccupied	-

⁵ Inert gas agent IG-541 contains 8% carbon dioxide and is approved by the U.S. EPA SNAP rules as a safe alternative to halon 1301 in total flooding fire protection systems. At elevated concentrations, however, carbon dioxide is not safe for human exposure and is lethal at fire extinguishing concentrations.

Agent exposure limits and system features for inert gas agents

The table below summarises the maximum agent concentration limits for personnel exposure up to 5 minutes, agent requirements for Class A and Class B fires, and some common system features.

Table 12: Inert Gas Agents Fixed System Features

Generic name	IG-541	IG-55	IG-01	IG-100
Agent exposure limits				
Max agent concentration where exposure is less than 5 min., vol % (1)	43	43	43	43
Max agent concentration where exposure is less than 3 min, vol % (2)	52	52	52	52
System requirements per m ³ of protected volume				
Class A hazard				
Agent gas volume, m ³ (3)	0.381	0.387	0.407	0.387
Cylinder storage volume, litre (4)	3.38	3.44	3.01	2.87
Cylinder volume relative to halon 1301 (5)	11.1	11.2	9.90	9.40
Class B hazard				
Agent gas volume, m ³ (3)	0.577	0.644	0.712	0.575
Cylinder storage volume, litre (4)	3.84	4.30	3.95	3.19
Cylinder volume relative to halon 1301 (5)	12.6	14.0	13.0	10.4
System Features				
Available cylinder sizes (typical), litre	16;67;80	16;67;80	16;67;80	16;67;80
Available cylinder pressures, bar	150 to 300	150 to 300	150 to 300	150 to 300
Nominal Discharge Time, seconds	60	60	60	60

Note 1: Corresponds to a residual oxygen concentration of 12 vol %.

Note 2: Corresponds to a residual oxygen concentration of 10 vol %.

Note 3: Based on minimum design concentrations in ISO/CD-14520, Parts 12 to 15 (2013).

Note 4: Approximate, for the 200 bar cylinder pressure.

Note 5: Halon 1301 cylinder volume per m³ hazard. See Note 4 of Table 7.

2.3 Carbon Dioxide

Carbon dioxide was used widely for fire protection prior to the introduction of halons. Owing to its toxicity, use of carbon dioxide in occupied or occupiable spaces requires the implementation of significant safety measures. Nonetheless, carbon dioxide has seen a resurgence in use subsequent to the halon production phase out, particularly in new commercial ship construction where halon 1301 once had a significant role. Minimum design concentrations for carbon dioxide are specified in national and international standards such as NFPA 12 and ISO 6183. The minimum design concentration for carbon dioxide systems is, typically, 35 vol % for Class B fuels and 34 vol % for Class A applications.

Carbon dioxide toxicity

Carbon dioxide is essentially chemically inert as a fire extinguishing gas. Carbon dioxide does, however, have significant adverse physiological effects when inhaled at concentrations above 4 vol %. The severity of physiological effects increases as the concentration of carbon dioxide in air increases. Exposure to carbon dioxide at concentrations exceeding 10 vol % poses severe health risks including risk of death. As such, atmospheres containing carbon dioxide at fire extinguishing concentrations are always lethal to humans. Precautions must always be taken to ensure that occupied spaces are not put at risk by ingress of carbon dioxide from a space into which the agent has been discharged.

The use of carbon dioxide is not recommended for total flooding of normally occupied spaces. NFPA 12 (2008) includes new restrictions on the use of carbon dioxide in normally occupied spaces. Safety precautions related to the use of carbon dioxide may also be found in ISO 6183 (2009).

Environmental factors of carbon dioxide

The carbon dioxide used in fire protection applications is not produced for this use. Instead, it is captured from an otherwise emissive use temporarily sequestering it until it is released. Thus, carbon dioxide from fire protection uses has no net effect on the climate.

The table below summarizes key attributes of carbon dioxide.

Table 13: Carbon Dioxide

Agent	Carbon dioxide, CO ₂
Efficacy	For use in unoccupied spaces Basic design concentration = 34 vol% for a “material factor” of 1. Design concentrations for specific combustible materials are determined by multiplying the basic design concentration by an applicable material factor. (1)
Toxicity	Progressively more severe physiological effects as exposure concentration increases, especially above 10 vol%. Carbon dioxide concentrations that exceed 17 vol% present an immediate risk to life. (2) Pre-discharge alarm and discharge time delay required.
Safety Characteristics	Liquefied compressed gas Storage pressure: High-pressure cylinder: 55.8 bar at 20 °C Low-pressure tanks (refrigerated): 21 bar at -18 °C Sublimes at -78.5 °C at atmospheric pressure; cold exposure hazard. Vapours are denser than air and can accumulate in low-lying spaces.
Environmental Characteristics	GWP = 1
Cost-Effectiveness, avg. for 500 to 5 000 m ³ volume (2003 data)	1

Note 1: See ISO 6183:2009

Note 2: See U.S. Environmental Protection Agency, “Carbon Dioxide as a Fire Suppressant: Examining the Risks,” February 2000.

2.4 Water Mist Technology

Water mist fire suppression technologies are described in national and international standards such as NFPA 750 *Standard on Water Mist Fire Protection Systems* and the FM Approvals Standard No. 5560 *Water Mist Systems*.

Water mist system technologies strive to generate and distribute within a protected space very small mist droplets which serve to extinguish flames by the combined effects of cooling and oxygen dilution by steam generated upon water evaporation. Technologies used to generate fine water mists include:

- Low pressure single fluid atomisation
- High pressure single fluid atomisation
- Dual-fluid atomization
- Hot water steam generation

Briefly, fine water mist relies on sprays of relatively small diameter droplets (less than 200 µm) to extinguish fires. The mechanisms of extinguishment include the following:

- Gas phase cooling
- Oxygen dilution by steam formation
- Wetting and cooling of surfaces, and
- Turbulence effects

The table below summarizes key attributes of water mist technology.

Table 14: Water Mist Technology

Agent	Water mist
Efficacy	For use in occupied spaces. Uses approximately 10 % of the total water quantity discharged by traditional sprinkler system to suppress fires, where tested.
Toxicity	None
Safety Characteristics	No adverse safety characteristics
Environmental Characteristics	No adverse characteristics
Cost-Effectiveness, avg. for a 3 000 m ³ application space	~2

Water mist systems offer some advantages due to their low environmental impact, ability to suppress three-dimensional flammable liquid fires under defined conditions, and reduced water application rates relative to automatic sprinklers in certain applications. More recent innovations include use of nitrogen with water mist to achieve inert gas extinguishing effects, and use of bi-fluid (air-water) nozzles to achieve ultrafine droplets and adjustable spray patterns (by varying the air-water ratio). The use of relatively small (10-100 µm) diameter water droplets as a gas phase extinguishing agent has been established for at least 40 years. Advances in nozzle design and improved theoretical understanding of fire suppression processes has led to the development of at least nine technologies for use in water mist fire suppression systems. Several systems have been approved by national authorities for use in relatively narrow application areas. To date, these applications include shipboard machinery spaces, combustion turbine enclosures, flammable and combustible liquid storage spaces as well as light and ordinary hazard sprinkler application areas.

Theoretical analysis of water droplet suppression efficiencies has indicated that a liquid water volume concentration on the order of 0.1 litre of water per cubic meter of protected space is sufficient to extinguish fires. This represents a potential of two orders of magnitude efficiency improvement over application rates typically used in conventional sprinklers. The most important aspect of water mist technology is the extent to which the mist spray can be mixed and

distributed throughout a compartment versus the loss rate by water coalescence, surface deposition, and gravity dropout. The suppression mechanism of water mist is primarily cooling of the flame reaction zone below the limiting flame temperature. Other mechanisms are important in certain applications; for example, oxygen dilution by steam has been shown to be important for suppression of enclosed 3-D flammable liquid spray fires.

The performance of a particular water mist system is strongly dependent on its ability to generate sufficiently small droplet sizes and distribute adequate quantities of water throughout the compartment. Factors that affect the ability of achieving that goal include droplet size and velocity, distribution, and spray pattern geometry, as well as the momentum and mixing characteristics of the spray jet and test enclosure effects. Hence, the required application rate varies by manufacturer for the same hazard. Therefore, water mist must be evaluated in the combined context of a suppression system and the risk it protects and not just an extinguishing agent.

There is no current theoretical basis for designing the optimum droplet size and velocity distribution, spray momentum, distribution pattern, and other important system parameters. This is quite analogous to the lack of a theoretical basis for nozzle design for total flooding, gaseous systems, or even conventional sprinkler and water spray systems. Hence, much of the experimental effort conducted to date is full-scale fire testing of particular water mist hardware systems which are designed empirically. This poses special problems for standards making and regulatory authorities.

There are currently two basic types of water mist suppression systems: single and dual fluid systems. Single fluid systems utilise water delivered at 7-200 bar pressure and spray nozzles which deliver droplet sizes in the 10 to 100 μm diameter range. Dual systems use air, nitrogen, or another gas to atomise water at a nozzle. Both types have been shown to be promising fire suppression systems. The major difficulties with water mist systems are those associated with design and engineering. These problems arise from the need to distribute and maintain an adequate concentration of mist throughout the space while momentum of hot fire gases, ventilation, gravity and water deposition loss on surfaces deplete the concentration. Engineering analysis and experimental programmes for specific mist products (with unique droplet distribution and concentration) are employed to minimise the uncertainty.

Physiological Effects of water mist. At the request of the US EPA, manufacturers of water mist systems and other industry partners convened a medical panel to address questions concerning the potential physiological effects of inhaling very small water droplets in fire and non-fire scenarios. Disciplines represented on the Panel included inhalation toxicology, pulmonary medicine, physiology, aerosol physics, fire toxicity, smoke dynamics, and chemistry, with members coming from commercial, university, and military sectors. The Executive Summary (draft "Water Mist Fire Suppression Systems Health Hazard Evaluation;" Halon Alternatives Research Corporation (HARC), US Army, NFPA; March 1995) states the following: "The overall conclusion of the Health Panel's review is that...water mist systems using pure water do not present a toxicological or physiological hazard and are safe for use in occupied areas. Thus, EPA is listing water mist systems composed of potable water and natural sea water as acceptable without restriction. However, water mist systems comprised of mixtures in solution must be submitted to EPA for review on a case-by-case basis".

Environmental factors of water mist. Water mist does not contribute to stratospheric ozone depletion or to greenhouse warming of the atmosphere. Water containing additives may, however, have other environmental contamination risks, e.g., foams, antifreeze and other additives.

2.5 Inert Gas Generators

Inert gas generators are pyrotechnic devices that utilise a solid material which oxidises rapidly, producing large quantities of carbon dioxide and/or nitrogen. Recent innovations include generators that produce high purity nitrogen or nitrogen and water vapour with little particulate content. The use of this technology to date has been limited to specialised applications such as dry bays on military aircraft. This technology has demonstrated excellent performance in these applications with space and weight requirements equivalent to those of halon 1301 and is currently being utilised in some US Navy aircraft applications. The table below summarizes key attributes of inert-gas generator agents.

Table 15: Inert Gas Generators

Agent	Inert gas by pyrotechnic generator
Efficacy	For use in occupied or unoccupied spaces depending on properties of emitted agent.
Toxicity	Toxicity depends on the type of gas generator. Guidance related to oxygen concentration reduction applicable to inert gas systems must be followed. Additional safety considerations required where discharged gas contains carbon dioxide.
Safety Characteristics	Potentially hot-gas discharge; potential hot surfaces of generator body. Insulating consideration required by generator manufacturer. Discharge of inert gases into an enclosure will cause a rise in pressure to a level that depends on enclosure venting characteristics.
Environmental Characteristics	No adverse characteristics
Cost-Effectiveness	Not available

Physiological effects of inert gas generator agents. The precise composition and properties of the gas produced will affect the response of exposed persons and are determinant factors regarding application in occupied or unoccupied areas. U.S. EPA SNAP has listed as acceptable a gas generator that produces relatively pure nitrogen for use in normally occupied spaces.

Environmental effects of inert gas generator agents. Gases emitted by these products do not contribute to stratospheric ozone depletion or to greenhouse warming of the atmosphere except to the extent that they emit carbon dioxide, if any.

2.6 Fine Solid Particulate Technology

Another category of technologies being developed and introduced are those related to fine solid particulates and aerosols. These take advantage of the well-established fire suppression capability of solid particulates, with potentially reduced collateral damage associated with traditional dry chemicals. This technology is being pursued independently by several groups and is proprietary. To date, a number of aerosol generating extinguishing compositions and aerosol extinguishing means have been developed in several countries. They are in production and are used to protect a range of hazards. The table below summarizes key attributes of fine solid particle agents (powders).

Table 16: Fine Solid Particles (Powders)

Agent	Fine solid particles
Efficacy	For use in normally unoccupied spaces on Class B fires.
Toxicity	Precautions require evacuation of spaces before discharge.
Safety Characteristics	<p>For establishments manufacturing the agent or filling, installing, or servicing containers or systems to be used in total flooding applications, United States EPA recommends the following:</p> <ul style="list-style-type: none"> - adequate ventilation should be in place to reduce airborne exposure to constituents of agent; - an eye wash fountain and quick drench facility should be close to the production area; - training for safe handling procedures should be provided to all employees that would be likely to handle containers of the agent or extinguishing units filled with the agent; - workers responsible for clean-up should allow for maximum settling of all particulates before re-entering area and wear appropriate protective equipment <p>Discharge of associated inert gases into an enclosure will cause a rise in pressure to a level that depends on enclosure venting characteristics.</p>
Environmental Characteristics	No adverse characteristics
Cost-Effectiveness	Not available

One principle of these aerosol extinguishants is in generating solid aerosol particles and inert gases in the concentration required and distributing them uniformly in the protected volume. Aerosol and inert gases are formed through a burning reaction of the pyrotechnic charge having a specially proportioned composition. An insight into an extinguishing effect of aerosol compositions has shown that extinguishment is achieved by combined action of two factors such as flame cooling due to aerosol particles heating and vaporizing in the flame front as well as a chemical action on the radical level. Solid aerosols must act directly upon the flame. Gases serve as a mechanism for delivering the aerosol towards the seat of a fire.

A number of enterprises have commercialised the production of aerosol generators for extinguishing systems that are installed at stationary and mobile industrial applications such as nuclear power station control rooms, automotive engine compartments, defence premises, engine compartments of ships, telecommunications/electronics cabinets, and aircraft nacelles.

Fine particulate aerosols have also been delivered in HFC/HCFC carrier gases. A wide range of research into aerosol generating compositions has been carried out to define their extinguishing properties, corrosion activity, toxicity, and effect upon the ozone layer as well as electronics equipment.

Solid particulates and chemicals have very high effectiveness/weight ratios. They also have the advantage of reduced wall and surface losses relative to water mist, and the particle size distribution is easier to control and optimise. However, there is concern of potential collateral damage to electronics, engines, and other sensitive equipment. Condensed aerosol generators, which produce solid particulates through combustion of a pyrotechnic material, are unsuitable for explosion suppression or inerting since pyrotechnic/combustion ignited aerosols can be re-ignition sources. These agents also have low extinguishing efficiency on smouldering materials. Technical problems including high temperature, high energy output of combustion generated aerosols and the inability to produce a uniform mixture of aerosol throughout a complex geometry remain to be solved.

Additional information on fine solid particulate technologies may be found in NFPA 2010 *Standard for Fixed Aerosol Fire Extinguishing Systems*.

Physiological effects of fine particle agents

There are several potential problems associated with the use of these agents. These effects include inhalation of particulate, blockage of airways, elevated pH, reduced visibility, and the products of combustion from combustion generated aerosols, such as HCl, CO, and NO_x. For these reasons, the majority of these technologies are limited to use in only unoccupied spaces.

Environmental effects of fine particle agents

Fine particulate aerosols themselves and associated inert gases from generators do not contribute to stratospheric ozone depletion or to greenhouse warming of the atmosphere. There may be ozone depletion or greenhouse gas effects, however, where aerosols are delivered with halocarbon carrier gases.

2.7 System Design Considerations for Total Flooding Agents

Care must be taken throughout the design process to assure satisfactory system performance. Hazard definition, nozzle location and design concentration must be specified within carefully defined limits. Further, a high degree of enclosure integrity is required. Design requirements are provided by national and international standards such as NFPA 2001 and ISO 14520. An outline of factors to be taken into consideration is given below:

2.7.1 Definition of the Hazard

- Fuel type(s)
- Fuel loading
- Room integrity (openings, ventilation, false ceilings, subfloors)
- Dimensions and Net Volume of the room
- Temperature extremes
- Barometric pressure (altitude above sea level for gas systems)

2.7.2 Agent Selection

- Statutory approvals
- Personnel safety
- Minimum concentration required (cup burner/full scale tests)
- Design concentration required with factor of safety
- NOAEL/LOAEL or limiting oxygen concentration. Is the agent design concentration within safe exposure limits over the range of feasible hazard temperatures and net volumes?
- Decomposition characteristics
- Replenishment availability

2.7.3 System Selection

- System intended for use with the agent selected
 - Pressures, elastomers, gauges, labels
- System has appropriate approvals as the result of third party testing
 - Strength tests (containers, valves, gauges, hoses, etc.)
 - Leakage tests
 - Cycle testing of all actuating components
 - Corrosion tests
 - Cylinder mounting device tests
 - Aging tests for elastomers
 - Flow tests (software verification, balance limitations)
 - Fire tests (nozzle area coverage, nozzle height limitations)
- System has documented design, installation, maintenance procedures

2.7.4 System Design

- Automatic detection and control
 - Type of detection (smoke, heat, flame, etc.)
 - Logic (cross zoned, priority designated)
 - Control system features
 - Local and remote annunciation

- Start up and shut down of auxiliary systems
- Primary and back-up power supply
- Manual backup and discharge abort controls
- Central agent storage, distributed or modular
- Electrical, pneumatic or electrical/pneumatic actuation
- Detector location
- Alarm and control devices location
- Class A (control loop) or Class B electrical wiring
- Electrical signal and power cable specifications
- Nozzle selection and location
- Piping distribution network with control devices
- Piping and other component hangers and supports
- Agent hold time and leakage
- Selection of an appropriate design concentration
- Agent quantity calculations
- Flow calculations
- Pipe size and nozzle orifice determination

2.7.5 System Installation

- Installed per design
- System recalculated to confirm "as built" installation
- Correct piping
 - Size
 - Routing
 - Number and placement of fittings
 - Pipe supports
 - Correct type, style, orifice size nozzle in each location
- Fan test to confirm tightness of protected volume and adequacy of pressure relief venting
- Acceptance functional test of full system without discharge
 - Test each detector's operation
 - Test system logic with detection operation
 - Test operation of auxiliary controls
 - Test local and remote annunciation
 - Test signal received at system valve actuators
 - Test system manual operators
- Test system abort discharge abilities

2.7.6 Post-installation Follow Up

- Integrity of the protected space does not change
 - Walls, ceiling and floor intact

- Any new openings sealed properly
- Net volume and temperature range of the space does not change
- Regular maintenance for detection, control, alarm and actuation system
- Regular verification of the agent containers' charged weight
- Regular cleaning of the detection devices
- Confirmation of back-up battery condition

3.0 Local Application Agents

3.1 General

Local application agents, also referred to as streaming agents, are used in portable fire extinguishers and fixed extinguisher units designed to protect specific hazards. The tables below summarize commercially available, technically proven alternatives to halons for local application fire protection using portable or fixed systems. Cost effectiveness is represented by an index benchmarked against the approximate cost of a portable carbon dioxide extinguisher unit that has a UL 10B rating. Acceptability of substitutes for halons as streaming fire extinguishing agents is also regulated by national agencies as addressed in section 2.0, above.

3.2 Carbon Dioxide (CO₂)

Carbon dioxide extinguishers use CO₂ stored as a liquefied compressed gas. Carbon dioxide is most suitable for use on fires involving flammable liquids. Carbon dioxide does not conduct electricity and can be used safely on fires involving live electrical circuits. In general, carbon dioxide extinguishers are less effective for extinguishing fires of ordinary combustibles such as wood, paper and fabrics.

The table below summarizes key attributes of carbon dioxide as a streaming agent.

Table 17: Carbon dioxide streaming agent

Agent	Carbon dioxide, CO ₂
Efficacy	For use on Class B fires Can be used on most electrically energized equipment fires.
Toxicity	High exposure risk where carbon dioxide gas accumulates in confined spaces that may be entered by personnel.
Safety Characteristics	Liquefied compressed gas Storage pressure: 55.8 bar at 20 °C Solid CO ₂ (“dry ice”) sublimates at -78.5 °C at atmospheric pressure. Presents a cold-exposure hazard. Vapours usually flow to floor level so personnel exposure risk is normally low.
Environmental Characteristics	GWP = 1
Cost-Effectiveness	1

3.3 Halocarbon Agents

Halocarbon streaming agents come close to matching all the desirable properties of halon. For example they are effective on both solid and liquid fuel fires and they permeate well avoiding secondary damage. However, in general, they are more expensive than traditional fire protection agents and, on average more agent is required than would be for halon 1211. The table below summarises type, composition, and environmental properties of halocarbon alternatives to halon 1211, also included for reference, for use as local application agents.

Table 18: Halocarbon Streaming Agents

Generic Name	Group	Storage State	Chemical Composition		Environmental Factors		
			Weight %	Species	ODP	100 year GWP (1)	Atmospheric Lifetime yr.
Halon 1211	Halon	LCG	100 %	CF ₂ ClBr	3	1,750	16
HFC-236fa	HFC	LCG	100 %	CF ₃ CH ₂ CF ₃	0	8,060	242
HFC-227ea	HFC	LCG	100 %	CF ₃ CHF ₂ CF ₃	0	3,350	38.9
FK-5-1-12	FK	Liquid	100 %	C ₆ F ₁₂ O	0	< 1	7 days
FIC-13I1	FIC (2)	LCG	100 %	CF ₃ I	.0001	0.4	0.005
HCFC Blend B	HCFC & PFC blend	CGS	> 96 %	HCFC-123	0.02	79	1.3
			< 4 %	Ar	0	0	n/a
			< 2 %	CF ₄	0	6,630	> 50,000

LCG - Liquefied Compressed Gas; ODP - Ozone Depletion Potential; GWP - 100-year Global Warming Potential; CGS - Compressed Gas in Solution

Note 1: Source: IPCC 5th WGI Assessment Report

Note 2: FIC-13I1 has B.P. = -23 °C.

Toxicity of halocarbon streaming agents. The toxicity of streaming agents is assessed based on the likely exposure of the person using the extinguisher. This is sometimes measured using breathing zone samples. All of the streaming agents in Table 18 are considered safe for normal use in non-residential and unoccupied applications. Use of some of these agents in confined spaces may be a cause for concern. In particular, FIC-13I1 has a NOAEL of 0.2 vol % and a LOAEL of 0.4 vol % and, as such, poses risks to personnel in confined spaces.

Environmental Factors of halocarbon streaming agents. The environmental factors for halocarbon streaming agent alternatives are the same as those discussed for halocarbon total flooding agents. Information on ODP, GWP and atmospheric lifetime are presented in the table below. Traditional streaming agents (e.g. water, aqueous salt solutions, dry chemical, and foam) do not present environmental concerns in the areas of ODP, GWP, or atmospheric lifetime but may offer other environmental risks associated with the use of additives, e.g., fluoro-surfactants.

The table below summarizes key attributes of halocarbon chemical streaming agents.

Table 19: Halocarbon chemical streaming agents

Agent	HCFC Blend B 96% HCFC-123 < 2% CF ₄ < 4% Argon	HFC-236fa	HFC-227ea	FK-5-1-12	FIC-1311 ⁶																																				
Efficacy	For use on Class A fires For use on Class B fires For use on fires involving electrified equipment																																								
Toxicity	Vapour toxicity low to moderate.				Vapour toxicity moderate to high.																																				
	Vapour exposure risk usually low. Some halogen acids form upon application to a fire. Dense vapour can accumulate in low spaces.																																								
Safety Characteristics	Pressurised hand-held container.																																								
Environmental Characteristics (1)	<table border="1"> <thead> <tr> <th></th> <th>ODP</th> <th>GWP</th> </tr> </thead> <tbody> <tr> <td>HCFC-123</td> <td>0.02</td> <td>79</td> </tr> <tr> <td>CF₄</td> <td>0</td> <td>6,630</td> </tr> <tr> <td>Argon</td> <td>0</td> <td>0</td> </tr> </tbody> </table>		ODP	GWP	HCFC-123	0.02	79	CF ₄	0	6,630	Argon	0	0	<table border="1"> <thead> <tr> <th></th> <th>ODP</th> <th>GWP</th> </tr> </thead> <tbody> <tr> <td></td> <td>0</td> <td>8,060</td> </tr> </tbody> </table>		ODP	GWP		0	8,060	<table border="1"> <thead> <tr> <th></th> <th>ODP</th> <th>GWP</th> </tr> </thead> <tbody> <tr> <td></td> <td>0</td> <td>3,350</td> </tr> </tbody> </table>		ODP	GWP		0	3,350	<table border="1"> <thead> <tr> <th></th> <th>ODP</th> <th>GWP</th> </tr> </thead> <tbody> <tr> <td></td> <td>0</td> <td><10</td> </tr> </tbody> </table>		ODP	GWP		0	<10	<table border="1"> <thead> <tr> <th></th> <th>ODP</th> <th>GWP</th> </tr> </thead> <tbody> <tr> <td></td> <td>0.4</td> <td>0.0001</td> </tr> </tbody> </table>		ODP	GWP		0.4	0.0001
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Cost-Effectiveness	Varies from about 1 to about 2																																								

Note 1: Source: IPCC 5th WGI Assessment Report

3.4 Dry Chemical Agents

Dry chemical extinguishers are of two types. “Ordinary” dry chemicals, usually formulations based on sodium or potassium bicarbonate, are suitable for fires involving flammable liquids and gases. “Multipurpose” dry chemicals, usually formulations of monoammonium phosphate (MAP), are suitable for use on fires of ordinary combustibles such as wood, paper and fabrics and fires involving flammable liquids and gases. Both ordinary and multipurpose dry chemicals may be safely used on fires where electrical circuits are present; however, after application dry chemical residue should be removed because in the presence of moisture it could provide an electrical path that would reduce insulation effectiveness. The table below summarizes key attributes of dry chemical streaming agents.

⁶ Principal known use of FIC-1311 is as a substitute for halons for fire protection of rim seals on floating roof petroleum tanks.

Table 20: Dry chemical streaming agents

Agent	Dry chemicals
Efficacy	For use on Class A fires: Multipurpose dry chemical For use on Class B fires: Ordinary dry chemical or multipurpose dry chemical For use on fires involving electrified equipment Dry chemical applied to some electrical or sensitive equipment may cause damage otherwise not caused by a fire.
Toxicity	Low. Precautions required to avoid inhalation of agent particles.
Safety Characteristics	Pressurised containers
Environmental Characteristics	Low environmental risk
Cost-Effectiveness	~ 0.2

3.5 Straight-Stream Water

Straight stream water is suitable for use on fires of ordinary combustibles such as wood, paper and fabrics only. This type of extinguisher is unsuitable for use in extinguishing fires involving liquids or gases and in fact could spread a flammable liquid fuel. Straight stream water extinguishers are unsafe for use on fires where energised electrical circuits are present. The table below summarizes key attributes of straight-stream water as a streaming agent.

Table 21: Water, straight stream

Agent	Water, straight-stream , ~9 litre
Efficacy	For use on Class A fires not involving electrified equipment or materials that are reactive with water (e.g. metals). Not suitable for Class B fires. Water applied to some electrical or sensitive equipment may cause damage otherwise not caused by a fire.
Toxicity	Non-toxic
Safety Characteristics	No adverse characteristics. Not suitable for use on electrified equipment.
Environmental Characteristics	No significant risk
Cost-Effectiveness	~0.5

3.6 Water Mist (spray)

Water spray extinguishers are most suitable for use on fires of ordinary combustibles such as wood, paper and fabrics. This type of extinguisher may be less effective on deep-seated fires. The spray stream is generally more effective on burning embers and may provide a limited capability for fires involving combustible liquid fuels. Some water spray extinguishers can be used on fires where live electrical circuits are present. Users should ensure that the extinguisher has been tested and certified before use on live electrical circuits. Some manufacturers have introduced “water mist” fire extinguishers into commerce. The table below summarizes key attributes of water mist or spray as a streaming agent.

Table 22: Fine water spray as a streaming agent

Agent	Water, fine spray
Efficacy	For use on Class A fires including use on electrified equipment up to 10 kV. Not suitable for use on materials that are reactive with water (e.g. metals). Not suitable for Class B fires. Water applied to some electrical or sensitive equipment may cause damage otherwise not caused by a localized fire.
Toxicity	Non-toxic
Safety Characteristics	No adverse characteristics
Environmental Characteristics	No significant risk
Cost-Effectiveness	~0.6 (~9 litre extinguisher unit; cost index compared to a 10B-rated CO ₂ unit)

3.7 Aqueous Salt Solutions

Aqueous solutions of certain salts are used in fire protection for certain types of hazards. Water containing certain dissolved salts has been found to be more effective than water alone in the extinguishment of fires. Potassium salts are usually employed. Examples include potassium acetate, potassium citrate, potassium formate, potassium lactate, and others, sometimes in combination, and with additives to inhibit corrosion, promote aqueous film-forming action to suppress vapor evolution from flammable liquids, and solution stability. Applications for aqueous salt solutions include fire protection for commercial cooking equipment and industrial vehicles. Some attributes of aqueous salt solution agents are summarized in the table below.

Table 23: Aqueous salt solutions streaming agents

Agent	Aqueous salt solutions, fine spray
Efficacy	For use on Class A fires not involving electrified equipment or materials that are reactive with water (e.g. metals). Suitability for use on Class B fires depends on formulation and means of delivery. Used on cooking oil fires where nozzle design limits splatter of hot oil. Salt solutions may cause damage to some electrical equipment not otherwise damaged by fire.
Toxicity	Varies from low to moderate.
Safety Characteristics	pH usually basic varying from 8 to 13. Possible short-exposure skin irritation depending on duration of exposure if wetted with agent.
Environmental Characteristics	No significant risk
Cost-Effectiveness	~0.7 to 1 (~9 litre extinguisher unit; cost index compared to a 10B-rated CO ₂ unit)

3.8 Aqueous Film Forming Foam (AFFF)

Extinguishers using water and AFFF additives may be more effective than those using clean water only on fires of ordinary combustibles such as wood, paper and fabrics. Additionally, water with AFFF additives will have improved ability, over water alone, to extinguish fires involving flammable or combustible liquids. Also, this agent has the ability to reduce the likelihood of ignition when applied to the liquid surface of an unignited spill. The aqueous film forming foam reduces vapour propagation from the flammable liquid.

Depending upon the stream pattern, this type of extinguisher may not be safe for use on fires where live electrical circuits are present.

“The table below summarizes key attributes of streaming agents employing AFFF. It should be noted that some currently-available AFFF agents contain surfactants consisting of perfluorinated eight-carbon (C8) molecular chains that are known to be biopersistent and bioaccumulative once released to the environment. The environmental impact of using AFFF agents containing C8 fluoro-surfactants must be weighed against the potential gain in efficacy when selecting a portable extinguisher for each specific application. A number of manufacturers have ceased or will cease production in 2015 of fluoro-surfactants containing the problematic C8 species. The performance properties of AFFF agents using reformulated fluorosurfactants should be verified.”

Table 24: Aqueous film-forming foam as a streaming agent

Agent	Aqueous film-forming foam (AFFF)
Efficacy	For use on Class A fires not involving electrified equipment or materials that are reactive with water (e.g. metals). For use on Class B fires.
Toxicity	Moderate.
Safety Characteristics	pH is approximately neutral, varying between about 6.5 and 8.
Environmental Characteristics	Uncontained run-off of agent poses risks of contamination of soil, streams, and rivers.
Cost-Effectiveness	~0.6 (~9 litre extinguisher unit; cost index compared to a 10B-rated CO ₂ unit)

3.9 Streaming Agents for Residential Use

Distinctions are often made by national bodies as to the acceptability of certain agent types in commercial and residential applications. Agents that have the potential of forming toxic byproducts in a fire are usually deemed unsuitable for residential use⁷. Based on this premise the suitability of agents for residential use is summarized in the table below.

⁷ For example, the U.S. EPA defines residential use to mean use by a private individual of a chemical substance or any product containing the chemical substance in or around a permanent or temporary household, during recreation, or for any personal use or enjoyment. Use within a household for commercial or medical applications is not included in this definition, nor is use in automobiles, watercraft, or aircraft.

Table 25: Suitability of fire extinguishing agent alternatives to halon 1211 for use in local application fire protection in residential applications

Substitute	Constituents	Suitable for Residential Use?
Surfactant Blend A	Mixture of organic surfactants and water	Yes
Carbon dioxide (1)	CO ₂	Yes
Water	H ₂ O	Yes
Water Mist Systems	H ₂ O	Yes
Foam	Aqueous film-forming foam (AFFF)	Yes
Dry Chemical	Formulations based on either monoammonium-phosphate (MAP) or sodium bicarbonate	Yes
Gelled Halocarbon/Dry Chemical Suspension	Halocarbon plus dry chemical plus gelling agent	Yes
HFC-227ea	CF ₃ CHF ₂ CF ₃	No
HFC-236fa	CF ₃ CH ₂ CF ₃	No
FK-5-1-12	CF ₃ CF ₂ C(O)CF(CF ₃) ₂	No
Hydrofluoro-polyethers	Hydrofluoro-polyethers	No
HCFC Blend B	HCFC-123, 95 mol% min; Argon, 0.2 mol% min; CF ₄ , 0.4 mol% min	No

Note 1: Avoid use in confined spaces.

3.10 Assessment of Alternative Streaming Agents

The important features of alternative, manually applied fire extinguishing agents are described below. In general portable extinguishers are only used on actual fires and can be readily directed at the burning material.

3.10.1 Effectiveness on ordinary combustibles

This parameter considers the ability of the agent to extinguish fires in ordinary solid combustibles, including cellulosic materials. These are called Class A fires and the extinguisher should carry a rating categorising its Class A performance.

3.10.2 Effectiveness on liquid fuel fires

This parameter considers the ability of the agent to extinguish liquid fuel fires (Class B). The extinguisher should carry a Class B rating.

3.10.3 Electrical conductivity

Minimal conductivity is important in fighting fires where electricity is involved.

3.10.4 Ability to Permeate

This parameter reflects the ability of the agent to extinguish fires in locations where direct application to the fuel surface or flame reaction zone is not possible, for example, in the hidden void space in a commercial airliner.

3.10.5 Range

This parameter reflects the ability of the agent to maintain a coherent effective stream over a modest distance.

3.10.6 Effectiveness to Weight Ratio

This parameter considers the relative fire suppression capability across all fuels per unit weight of agent.

3.10.7 Secondary Damage

This category refers to the “clean agent” aspects of the agents, i.e., secondary damage caused by the suppressant agent itself.

3.10.8 Selection of an Alternative Streaming Agent

The relative ratings for each parameter have not been rigorously derived and final selection depends on detailed knowledge of the risk to be protected. Some characteristics of several types of streaming agents are summarised in the table below.

Table 26: Portable fire extinguisher capability comparison

Agent Type	Ordinary Combustibles	Flammable Liquids	Suitable on Energised Electrical Hazards	Ability to Permeate	Stream Range	Effective Weight	Secondary Damage
CO ₂	Poor	Fair	Yes	Good	Fair	Poor	Good
Multi-purpose Dry Chemical	Good	Good	Yes	Fair	Good	Good	Poor
AFFF	Good	Fair	No	Poor	Good	Poor	Poor
Water Stream	Good	Poor	No	Poor	Good	Poor	Poor
Water Mist	Good	Fair	Yes	Fair	Fair	Fair	Fair
Halocarbon	Good	Good	Yes	Good	Good	Good	Good
Halon 1211	Good	Good	Yes	Good	Good	Good	Good
Sodium Bicarbonate Dry Chemical	Poor	Good	Yes	Fair	Good	Good	Poor
Potassium Bicarbonate Dry Chemical	Poor	Good	Yes	Fair	Good	Good	Poor

3.11 New and Emerging Technologies

Manufacturers of fire extinguishing agents and systems continue to develop and offer innovative products to serve as alternatives to halon 1301 and halon 1211 for total flooding and local application uses.

3.11.1 Halogenated Chemical Agents

C7 Fluoroketone, FK-6-1-14. This substitute is a blend of two C7 isomers: 55 – 65% of 3-pentanone, 1,1,1,2,4,5,5,5-octafluoro-2,4-bis(trifluoromethyl), CAS 813-44-5, with balance consisting of 3-hexanone, 1,1,1,2,4,4,5,5,6,6,6-undecafluoro-2-(trifluoromethyl), CAS 813-45-6. This product has been found acceptable under the U.S. EPA SNAP program for use as a streaming agent subject to narrow use limits that require that C7 fluoroketone be used only in nonresidential applications.

Low-GWP chemicals. One manufacturer has announced development of low-GWP chemicals for use as fire extinguishants. The manufacturer has not announced the chemical identities of these products but has disclosed some information summarised in the table below.

Table 27: Properties of developmental halocarbon agents with low GWP

Product	Flooding agent	Streaming agent #1	Streaming agent #2
Boiling point, °C	31	31	18
Liquid density, kg/m ³	1300	1380	1300
MDC, Class A, vol %	5.6	6.1	4.8
MDC, Class B, vol %	6.9	6.9	6.2
NOAEL, vol %	10	1.25	2.5
LOAEL, vol %	12.5	2.5	>2.5
ODP	0	0	0
100 yr. GWP (est.)	<2	<20	<20

Unsaturated hydrobromofluorocarbon, (HBFC). The chemical 3,3,3-trifluoro-2-bromo -prop-1-ene, CAS 1514-82-5 has been the subject of study as a fire extinguishant since before 2000. For brevity this chemical is referred to as “2-BTP.” It has been submitted to the U.S. EPA for review under the SNAP programme for use as a streaming agent. While 2-BTP does contain bromine, as do halons, this chemical has a very short atmospheric lifetime (about 7 days), an ODP of 0.0028 and a GWP of 0.26. As such, this chemical is not deemed as a potentially significant contributor

to ozone depletion or global warming. This product has been the subject of study for possible use as a streaming agent^[8,9, 10] in aircraft portable extinguishers.

Phosphorous tribromide. PBr_3 is a clear liquid with a boiling point of 173 °C. It reacts vigorously with water liberating HBr and phosphoric acid and is, therefore, a toxic substance at ambient conditions. Though the agent contains bromine, it poses little risk to stratospheric ozone. The agent decomposes rapidly in the atmosphere and the HBr formed is quickly eliminated by precipitation. PBr_3 is an effective fire extinguishant in part due to its bromine content. Given its high boiling point, and low volatility, this agent must be delivered as a spray or mist into the fire zone in order to be effective. It has been commercialised for use as a fire extinguishant in one small aircraft engine application.

Water mist technologies continue to evolve. Recently commercialised innovations include:

- New atomisation technology using two-fluid system (air and water) to create ultrafine mist with spray features that are adjustable by changing the flow ratio of water to air or nitrogen.
- Water mist combined with nitrogen to gain extinguishing benefits of both inert gas and water mist

Each approach to generating fine water mists has its own advantages and drawbacks. Additional comments on water mist systems are given in Sections 2.3 and 3.6.

4.0 Conclusions

Alternative extinguishing agents and technologies are available for nearly all new fire protection applications that previously employed halons. A current (2014) exception is the fire protection in cargo bays of civil aviation, where none have passed the International Aircraft Systems Fire Protection Working Group Minimum Performance Standard (MPS) for cargo bays. For some legacy systems used in military aviation and vehicles, and in oil and gas production facilities, retrofit with current halon alternatives is not technically or economically feasible at this time.

5.0 Sources

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FM 5560, Approvals Standard for Water Mist Systems. The latter 296 page document is available at no charge from the following website.
<http://www.fmglobal.com/assets/pdf/fmapprovals/5560.pdf>

⁸ See Morrison

⁹ See Colton

¹⁰ See Madden

Halon Alternatives Research Corp., PBPK Model, ISO 14520-1, Annex G, 2nd Edition, 2006, <http://www.harc.org/pbpkharc.pdf>

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