MONTREAL PROTOCOL
ON SUBSTANCES THAT DEPLETE
THE OZONE LAYER

UNEP

HALONS TECHNICAL OPTIONS COMMITTEE

Technical Note #1 – Revision 3

New Technology Halon Alternatives

Montreal Protocol
On Substances that Deplete the Ozone Layer

United Nations Environment Programme (UNEP)
Halons Technical Options Committee
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1.0 Fire Protection Alternatives to Halon

The following information is a minor update of that which can be found in the 2006 Assessment Report of the Halon Technical Options Committee.

1.1 Introduction

Halons are 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 were phased out of production under the Montreal Protocol countries in 1994 except in Article 5(1) countries where continued production of halons is permitted through 2009. 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 in portable fire extinguishing units for use in what are called “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 virtually every fire and explosion protection application once served by halons. Halon 2402 has been used in both total flooding and streaming agent applications.

Selection of the best fire protection method in the absence of halons is often a complex process. Either alternative gaseous fire extinguishing agents, so called in-kind alternatives, or not-in-kind alternatives may successfully replace 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. Several clean agents and new “not-in-kind” alternative technologies have been introduced to the market. The purpose of this document is to provide a brief review of the types of alternatives that are available, including information on physical and chemical characteristics, fire protection capabilities, toxicity, and key environmental parameters.

Since publication of Revision 2 of Technical Note 1, there have been some changes made to national and international fire protection standards that affect some of the measures of performance and guidelines for use of the agents described in this note.

- International standards recognize Class A fire hazards involving specific arrangements of electrified equipment may pose additional extinguishing challenges and re-ignition risks. In such cases higher minimum agent design concentrations are recommended.
- New procedures have been developed for determining safe personnel exposure guidelines where halocarbon agents are employed in occupied spaces. These procedures are based on what is referred to as the PBPK (physiologically-based

pharmacokinetic) model where exposure time is considered in addition to the NOAEL and LOAEL values of an agent.

- Both national and international standards 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 20% in some standards and 30% in others. 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.

<u>Total Flooding Applications.</u> A number of gaseous fire extinguishing agent technologies have been commercialized as alternatives to halon 1301 for use in total flooding applications. These are summarized in Table 1-1.

Several agents listed in Table 1-1 have been approved for use in normally occupied spaces. These agents include the named inert gas agents, HFC agents, perfluoroketone agent, gaseous agents containing particulate solids and HCFC Blend A. 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 presented in Table 1-4 for gaseous halocarbon agents without powder additives or Table 1-9 for inert gas agents, below. The United States Environmental Protection Agency, under the Significant New Alternatives Policy (SNAP) program, has reviewed a number of materials as substitutes for halons as fire extinguishing agents. The approval status of a number of such alternatives for use in total flooding systems and as streaming agents may be found at the EPA website:

http://www.epa.gov/spdpublc/snap/fire/lists/index.html.

Agents listed in Table 1-1 that are not suitable for use in occupied spaces include carbon dioxide, FIC-13I1, FIC-217I1, HCFC-124, and the aerosol powders.

In addition to gaseous agents, powders, and mixtures of these, a number of other technologies have been evaluated for fire extinguishing applications where halon 1301 might have formerly been used. These include water-foam technologies and several types of 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 atomization
- High-pressure single fluid atomization
- Dual-fluid atomization
- Hot water steam generation

Table 1-1 Gaseous Fire Extinguishing Agent Alternatives to Halons for Use in Total Flooding Applications

Agent	Composition
Inert Gases	
• IG-01	Argon, Ar
• IG-100	Nitrogen, N_2
• IG-541	Nitrogen, 52 vol. %; Argon, 40 vol. %; Carbon dioxide, 8 vol.%
• IG-55	Nitrogen, 50 vol. %; Argon, 50 vol. %
Carbon dioxide	Carbon dioxide, CO_2
Hydrofluorocarbons	
• HFC-125	C_2HF_5 – Pentafluoroethane
• HFC-23	CHF_3 - Trifluoromethane
• HFC-227ea	CF_3CHFCF_3 - 1,1,1,2,3,3,3-heptafluoropropane
• HFC-236fa	$CF_3CH_2CF_3$ - 1,1,1,3,3,3-hexafluoropropane
• HFC Blend B	HFC-134a, CH_2FCF_3, 1,1,1,2-tetrafluoroethane, 86 wt% HFC-125, C_2HF_5, pentafluroethane, 9 wt% Carbon dioxide, CO_2, 5 wt%
Perfluoroketone	
• FK-5-1-12	$CF_3CF_2(O)CF(CF_3)_2$ – Dodecafluoro-2-methylpentan-3-one
Iodofluorocarbon	
• FIC-13**I**1	CF_3I – Iodotrifluoromethane
• FIC-217**I**1	C3IF7 – Iodoheptafluoropropane
Hydrochlorofluorocarbons	
• HCFC-124	$CHFClCF_3$, 1-Chloro-1,2,2,2-tetrafluoroethane
• HCFC Blend A	HCFC-22, $CHClF_2$ - Chlorodifluoromethane, 82 wt % HCFC-124, $CHClF\text{-}CF_3$,1-Chloro-tetrafluoroethane, 9.5 wt% HCFC-123, $CHCl2\text{-}CF_3$, 1,1-dichloro-trifluoroethane, 4.75 wt% isopropenyl-1-methylcyclohexane, 3.75 wt%
Gaseous Agents Containing Particulate Solids	
• HFC227-BC	• HFC-227ea with 5 wt% sodium bicarbonate added.
• Gelled mixture of HFC plus dry chemical additive.	• HFC-125 plus ammonium polyphosphate or sodium bicarbonate • HFC-227ea plus ammonium polyphosphate or sodium bicarbonate • HFC-236fa plus ammonium polyphosphate or sodium bicarbonate
Aerosol Powders	
• Powdered Aerosol A	• Proprietary formulation
• Powdered Aerosol C	• Proprietary formulation

Each approach to generating fine water mists has its own advantages and drawbacks. Additional comments on water mist systems are given in Section 1.2.4.

Local Application. Extinguishing agents suitable for use as alternatives for halon 1211 are listed in Table 1-2.

Table 1-2 Fire Extinguishing Agent Alternatives to Halon 1211 for Use in Local Application Fire Protection

Agent	Comment
• HCFC Blend B	Blend of HCFC-123 and two additives
• HCFC Blend C	55% HCFC-123, 31% HFC-124, 10% HFC-134a, 4% d-Limonene
• HCFC Blend D	HCFC-123 plus proprietary additive
• HFC-236fa	$CF_3CH_2CF_3$ - 1,1,1,3,3,3-hexafluoropropane
• HFC-227ea	CF_3CHFCF_3 - 1,1,1,2,3,3,3-heptafluoropropane
• HCFC-123	$CHCl_2CF_3$, 1,1-Dichloro-2,2,2-trifluoroethane
• HCFC-124	$CHFClCF_3$, 1-Chloro-1,2,2,2-tetrafluoroethane
• Gelled Halocarbon / Dry Chemical Suspension	Halocarbon plus dry chemical plus gelling agent
• Surfactant Blend A	Mixture of organic surfactants and water
• Carbon Dioxide	Carbon dioxide, CO_2
• Dry chemical	Several product types based on different base chemistries including • BC powder - Sodium bicarbonate • ABC powder - Monoammoniumphosphate • Purple K - Potassium bicarbonate • Others
• Foam	Numerous aqueous foam chemistries and variations
• Water	Hand-held portable water fire extinguisher

1.2 Alternatives to Halon 1301 for Total Flooding Fire Protection using Fixed Systems

1.2.1 Halocarbon Agents (without powder additives)

Halocarbon agents share several common characteristics, with the details varying among products. Common characteristics include the following:

1.) All are electrically non-conductive;
2.) All are clean agents, meaning that they vaporize readily and leave no residue;
3.) All are stored as liquids or as liquefied compressed gases either as single component agents or as multi-component mixtures;
4.) All can be stored and discharged from fire protection system hardware that is similar to that used for halon 1301;
5.) All (except HFC-23) use nitrogen super-pressurization for discharge purposes;
6.) All (except CF_3I) are less efficient fire extinguishants than halon 1301;

7.) All, upon discharge, vaporize when mixed with air (except HCFC Blend A which contains 3.75% of a non-volatile liquid). Many require additional care relative to nozzle design; and

8.) All (except CF_3I) produce more decomposition products, primarily hydrogen fluoride (HF), than halon 1301 given similar fire type, size, and discharge time.

These agents differ widely in areas of toxicity, environmental impact, storage weight and volume requirements, cost, and availability of approved system hardware. Each of these categories will be discussed for each agent in the following sections.

1.2.1.1 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 which 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 pharmico-kinetic 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).

Table 1-4 summarizes the toxicity information[1] available for each chemical.

1.2.1.2 Environmental Factors

The primary environmental factors to be considered for halocarbon agents are ozone-depletion potential (ODP), global-warming potential (GWP), and atmospheric lifetime. These factors are summarized in Table 1-5. It is important to select the fire 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. PFCs, in particular, represent an unusually severe potential environmental impact due to the combination of extremely long atmospheric lifetime and high GWP.

[1] The principal basis for assessing the safety of gaseous halocarbon agents is cardiac sensitivity. A more complete discussion on the PBPK model may found at http://www.harc.org/pbpkharc.pdf.

International agreements and individual actions by national governments may affect future availability of these compounds and subsequent support for installed fire protection systems that utilize them. Some examples are presented below:

- HCFCs used in fire protection are scheduled for a production and consumption phase out under the Montreal Protocol in 2020 in developed countries and 2030 in developing countries.
- The Kyoto Protocol has identified carbon dioxide, methane, nitrous oxide and the fluorochemicals HFCs, PFCs and SF6 as the basket of six gases primarily responsible atmospheric greenhouse effects and potentially subject to emission controls. All uses of fluorochemicals represent less than 2% of current worldwide greenhouse gas emissions on a carbon-equivalency basis.

Table 1-3 Physical Properties of Gaseous Fire Extinguishing Agent Alternatives to Halons Used in Total Flooding Applications

Generic Name	Vapour Pressure @ 20º C, bar	k1 m^3/kg (1)	k2 $m^3/kg/^oC$ (1)	Vapour Density, @ 20ºC & 1 atm, kg/m^3	Liquid Density @ 20º C, kg/m^3
Halon 1301	12.90	0.1478	0.00057	6.283	1,572
HCFC Blend A	8.30	0.2413	0.00088	3.862	1,200
HCFC-124	3.30	0.1575	0.00066	5.858	1,373
HFC-23	41.83	0.3164	0.00122	2.934	807
HFC-125	12.10	0.1825	0.00073	5.074	1,218
HFC-227ea	3.91	0.1269	0.00052	7.283	1,407
HFC-236fa	2.30	0.1413	0.00057	6.549	1,377
FIC-13I1	4.65	0.1138	0.00050	8.078	2,096
FK-5-1-12	0.33	0.0664	0.000274	13.912	1,616
HFC Blend B	13.03	0.2172	0.0009	4.252	1.190

Note 1: Agent vapour specific volume $s = k1 + k2 \bullet t$, m^3/kg at an atmospheric pressure of 1.03 bar where t is the vapour temp. in ºC. Vapour density = 1/s.

Table 1-4 Gaseous Fire Extinguishing Agent Alternatives to Halons Used in Total Flooding Applications Minimum Extinguishing Concentrations and Agent Exposure Limits

Generic Name **ISO standard reference**	**Minimum Design Conc., Class A Fire Vol. % (1)**	**Minimum Design Conc., Higher Hazard Class A Fire Vol. % (8)**	**Minimum Design Conc., Class B Fire Vol. % (1)**	**Inerting Conc. Methane/Air, Vol. %**	**NOAEL Vol. % (2)**	**LOAEL Vol. % (2)**
Halon 1301	5.0 (3)	5.0 (3)	5.0 (3)	4.9	5	7.5
HCFC Blend A ISO 14520-6	7.8	12.4	13.0	20.1	10	>10
HCFC-124 (5, 6)	-	-	8.7 (4)	-	1	2.5
HFC-23 ISO 14520-10	16.2	16.3	16.4	22.2	30	>50
HFC-125 ISO 14520-8	11.2	11.5	12.1	-	7.5	10
HFC-227ea ISO 14520-9	7.9	8.5	9.0	8.8	9	10.5
HFC-236fa ISO 14520-11	8.8	9.3	9.8	-	10	15
FIC-13I1 (5) ISO 14520-2	4.6	4.6	4.6	7.15 propane	0.2	0.4
FK-5-1-12 ISO 14520-5	5.3	5.6	5.9	-	10	>10
HFC Blend B (5, 7)	14.7	14.7	14.7	-	5	7.5

Note 1: Design concentration = Extinguishing concentration x 1.3, the minimum permitted by ISO 14520.

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 (2004) 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: HCFC-124 data from 1999 revision of this report.

Note 5: Not approved for use in occupied spaces.

Note 6: These agents are not generally supplied in new suppression systems but may be found in legacy systems.

Note 7: 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 8: The minimum design concentration for Higher Hazard Class A fuels is the higher of the Surface Class A or 95% of the Class B minimum design concentration.

Table 1-5 Gaseous Fire Extinguishing Agent Alternatives to Halons Used in Total Flooding Applications Environmental Factors

Generic Name	Ozone Depletion Potential	Global Warming Potential, 100 yr. (1)	Atmospheric Life Time, yr. (1)
Halon 1301	10	6,900	65
HCFC Blend A	HCFC-22 – 0.055 HCFC-124 – 0.022 HCFC-123 – 0.02	HCFC-22 – 1,700 HCFC-124 – 620 HCFC-123 - 120	HCFC-22 – 11.9 HCFC-124 – 6.1 HCFC-123 – 1.4
HCFC-124	0.022	620	6.1
HFC-23	0	12,000	260
HFC-125	0	3,400	29
HFC-227ea	0	3,500	33
HFC-236fa	0	9,400	220
FIC-13I1	0.0001	1	0.005
FK-5-1-12	0	1	0.01
HFC Blend B	HFC-134a – 0 HFC-125 - 0	HFC-134a – 1,300 HFC-125 – 3,400	HFC-134a – 13.8 HFC-125 - 29

Note 1: Source: IPCC Third Assessment Report (2001) except for FK-5-1-12 for which data was supplied by the manufacturer.

Table 1-6 Gaseous Fire Extinguishing Agent Alternatives to Halons Used in Total Flooding Applications Halocarbon Agent Quantity Requirements 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	0.331	1.000	0.210	1,082	1.00	25 or 42
HCFC Blend A	0.327	0.988	0.272	900	1.19	25 or 42
HCFC-124	0.558	1.689	0.407	1,140	1.60	25
HFC-23	0.567	1.716	0.703	860	2.16	42
HFC-125	0.640	1.936	0.525	831	2.52	25
HFC-227ea	0.625	1.890	0.444	1,150	1.78	25 or 42
HFC-236fa	0.632	1.911	0.459	1,200	1.72	25 or 42
FIC-13I1	0.389	1.178	0.186	1,680	0.76	25
FK-5-1-12	0.779	2.355	0.482	1,680	1.52	25
HFC Blend B	0.733	2.216	0.616	930	2.58	25 or 42

Note 1: Halon alternative agent quantities based on 1.3 safety factor.
Note 2: Mass and volume ratios based on "Minimum Class A Fire Design Concentrations" from Table 1-4.
Note 3: Fill density based on 25 bar pressurization except for HFC-23.
Note 4: Agent cylinder volume per m^3 protected volume = (Agent Mass, kg/m^3 protected volume)/ (Maximum Fill Density, kg/m^3 cylinder) = ($V_{CYL}/V_{ProtVol}$). For halon 1301 cylinder volume per m^3 hazard = (0.331 kg/m^3 hazard)/ (1082 kg/m^3 cylinder) = 0.0003059 m^3 cylinder /m^3 protected volume.

Table 1-7 Gaseous Fire Extinguishing Agent Alternatives to Halons Used in Total Flooding Applications Halocarbon 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	1.000	0.210	1,082	1.00	25 or 42
HCFC Blend A	0.577	1.746	0.481	900	2.10	25 or 42
HCFC-124	0.558	1.689	0.407	1,140	1.60	25
HFC-23	0.576	1.741	0.713	860	2.19	42
HFC-125	0.698	2.113	0.573	831	2.75	25
HFC-227ea	0.720	2.179	0.512	1,150	2.05	25 or 42
HFC-236fa	0.712	2.152	0.517	1,200	1.94	25 or 42
FIC-13I1	0.389	1.178	0.186	1,680	0.76	25
FK-5-1-12	0.872	2.638	0.540	1,680	1.70	25
HFC Blend B	0.733	2.216	0.616	930	2.58	25 or 42

Note 1: Nominal maximum discharge time is 10 seconds in all cases.
Note 2: Mass and volume ratios based on "Minimum Class B Fire Design Concentrations" from Table 1-4.
Note 3: Fill density based on 25 bar pressurization except for HFC-23.
Note 4: Agent cylinder volume per m^3 of protected volume = (Agent Mass, kg/m^3 of protected volume)/(Maximum Fill Density, kg/m^3 cylinder) = ($V_{CYL}/V_{ProtVol}$). For halon 1301 cylinder volume per m^3 of protected volume = (0.331 kg/m^3 hazard)/ (1082 kg/m^3 cylinder) = 0.0003059 m^3 cylinder/m^3 of protected volume.

1.2.2 Carbon Dioxide

Carbon dioxide, used widely for fire protection prior to the introduction of halons, 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.

1.2.2.1 Toxicity effects

Carbon dioxide is essentially chemically inert as a fire extinguishing gas. Carbon dioxide does, however, have significant adverse physiologically 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 assure that occupied spaces are not put at risk by ingress of carbon dioxide from a space into which the agent has been discharged. A more complete discussion of the health and safety risks of carbon dioxide can be found in “Carbon Dioxide as a Fire Suppressant: Examining the Risks” and “Review of the Use of Carbon Dioxide Total Flooding Fire Extinguishing Systems,” which can be found at the EPA website:

http://www.epa.gov/spdpublc/snap/fire/index.html.

1.2.3 Inert Gas Agents

There have been at least four inert gases or gas mixtures commercialized as clean total flooding fire suppression agents. Inert gas agents are typically used at design concentrations of 35-50 vol. % which reduces the ambient oxygen concentration to between 14% to 10% by volume, 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 commercialized since 1990 consist of nitrogen, argon, blends of nitrogen and argon. One blend contains 8% carbon dioxide.

The features of the commercialized inert gas agents are summarized in Tables 1-8 and 1-9. 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:

1.) They are not liquefied gases. They are stored as high pressure gases and hence require high pressure storage cylinders which may have storage volume and weight impact.
2.) These systems use pressure reducing devices at or near the discharge manifold. This reduces the pipe thickness requirements and alleviates concerns regarding high pressure discharges.
3.) Discharge times are on the order of one to two minutes. This may limit some applications involving very rapidly developing fires.
4.) Inert gas agents are not subject to thermal decomposition and hence form no by-products.

Table 1-8 Inert Gas Agents for Fixed Systems
Agent Properties & System Features

Generic name	IG-541 ISO 14520-15	IG-55 ISO 14520-14	IG-01 ISO 14520-12	IG-100 ISO 14520-13
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
Properties				
k1, m^3/kg (1)	0.65799	0.6598	0.5612	0.7998
k2, m^3/kg/deg 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^{o}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. Higher Hazard Class A fire design conc. is the higher of the Surface Class A or 95% of the Class B min. design conc., vol %	39.9	45.1	48.4	41.5
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 s = k1 + k2 x t, m3/kg at an atmospheric pressure of 1.03 bar where t is the vapour temperature in deg C. Vapour density = 1/s.

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

1.2.3.1 Physiological Effects

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% carbon dioxide[2], which is intended to increase blood oxygenation and cerebral blood flow in low oxygen atmospheres.

1.2.3.2 Environmental Factors

Inert gas agents are neither ozone depleting substances nor greenhouse gases and, as such, pose no risk to the environment.

Table 1-9 Inert Gas Agents Fixed System Features

Generic name	IG-541	IG-55	IG-01	IG-100
Agent exposure limits				
Max unrestricted agent conc., vol. % (1)	43	43	43	43
Max restricted agent conc., vol. % (2)	52	52	52.	52
System requirements per m^3 of protected volume				
Class A hazard				
Agent gas volume, m^3	0.457	0.529	0.509	0.494
Cylinder storage volume, litre (3)	3.04	3.53	2.83	2.75
Cylinder volume relative to halon 1301 (4)	10.0	11.5	9.3	9.0
Class B hazard				
Agent gas volume, m^3	0.531	0.643	0.715	0.574
Cylinder storage volume, litre (3)	3.54	4.29	3.97	3.19
Cylinder volume relative to halon 1301 (4)	11.6	14.0	13.0	10.4
System Features				
Nominal Discharge Time, seconds	60	60	60	60
Cylinder pressure, bar	150 or 200	150 or 200	180	180 or 240

Note 1: Corresponds to a residual oxygen concentration of 12 Vol. %.
Note 2: Corresponds to a residual oxygen concentration of 10 Vol. %.
Note 3: Approximate, for the minimum indicated cylinder pressure.
Note 4: Halon 1301 cylinder volume per m3 hazard. See Note 4 of Table 1-6.

[2] 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.

1.2.4 Water Mist Technology

One of the non-traditional halon replacements which has been developed and commercialized is fine 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*. The latter 249 page document is available at no charge from the following website:

http://www.fmglobal.com/approvals/resources/approvalstandards/5560.pdf.

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

Water mist systems have attracted a great deal of attention and are under active development due primarily to their low environmental impact, ability to suppress three-dimensional flammable liquid fires, and reduced water application rates relative to automatic sprinklers. The use of relatively small (10-100 μ) diameter water droplets as a gas phase extinguishing agent has been established for at least 40 years. Recent advances in nozzle design and improved theoretical understanding of fire suppression processes has led to the development of at least nine 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 water liquid volume concentrations on the order of 0.1 L 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. This depends on the droplet size, 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 utilize water delivered at 40-200 bar pressure and spray nozzles which deliver droplet sizes in the 10 to 100 μ diameter range. Dual systems use air, nitrogen, or other gas to atomize water at a nozzle. Both types have been shown to be promising fire suppression systems. It is more difficult to develop single phase systems with the proper droplet size distribution, spray geometry, and momentum characteristics. This difficulty is offset by the advantage of requiring only a high pressure water source versus water and atomizer gas storage.

The major difficulties with water mist systems are those associated with design and engineering. These problems arise from the need to distribute the mist throughout the space while gravity and agent deposition loss on surfaces deplete the concentration and the need to generate, distribute, and maintain an adequate concentration of the proper size droplets. Engineering analysis and evaluation of droplet loss and fallout as well as optimum droplet size ranges and concentrations can be used effectively to minimize the uncertainty and direct the experimental program.

1.2.4.1 Physiological Effects

At the request of the United States Environmental Protection Agency, 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;” 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.”

1.2.4.2 Environmental Factors

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

1.2.5 Inert Gas Generators

Inert gas generators utilize a solid material which oxidizes rapidly, producing large quantities of CO_2 and/or nitrogen. The use of this technology to date has been limited to specialized 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 utilized in some U.S. Navy aircraft applications.

1.2.5.1 Physiological Effects

Applications to date have included normally unoccupied areas only. The precise composition of the gas produced will obviously affect the response of exposed persons. Significant work is required to expand application of this technology to occupied areas.

1.2.5.2 Environmental Effects

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.

1.2.6 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.

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 aerosol towards the seat of a fire.

A number of enterprises have commercialized the production of aerosol generators for extinguishing systems which 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. The compositions are low in cost and use relatively simple hardware. 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 optimize. 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*.

1.2.6.1 Physiological Effects

There are several potential problems associated with the use of these agents. While none of these problems has been proven, they remain potential concerns particularly in the protection of occupied spaces. 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.

1.2.6.2 Environmental Factors

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 environmental ozone depletion or greenhouse gas effects, however, where aerosols are delivered with halocarbon carrier gases.

1.3 System Design Considerations for Fixed Systems

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:

1.3.1 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)

1.3.2 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

1.3.3 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

1.3.4 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

1.3.5 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

1.3.6 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

1.4 Alternatives for Portable Extinguishers

1.4.1 Traditional Streaming Agents

1.4.1.1 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 energized electrical circuits are present.

1.4.1.2 Water Fog (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 very 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.

1.4.1.3 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 AFF 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.

1.4.1.4 Carbon Dioxide (CO_2)

Carbon dioxide extinguishers use CO_2 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.

1.4.1.5 Dry Chemical

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.

1.4.2 Halocarbon Agents

Information on halocarbon streaming agents is contained in Table 1-10. These agents come closest 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.

1.4.2.1 Toxicity

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 discussed above are considered safe for normal use. Use of some of these agents in confined spaces may be a cause for concern.

1.4.2.2 Environmental Factors

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 Table 1-10. Traditional streaming agents 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., fluorosurfactants.

Table 1-10 Halocarbon Streaming Agents for Portable Fire Extinguishers

	Physical Characteristics				Environmental Factors		
Generic Name	Group	Storage State	Chemical Composition Weight %	Chemical Composition Species	ODP**	GWP*** 100 yr. (1)	Atmospheric Lifetime yr. (1)
Halon 1211	Halon	LCG*	CF_2ClBr		3	1,300	11
HCFC Blend B	HCFC &	CGS****	>96%	HCFC-123	0.02	120	1.4
	PFC Blend		<4%	CF_4	0	5,700	50,000
			<4%	Argon	0	n/a	n/a
HCFC Blend E	HCFC	LCG*	90%	HCFC-123	0.02	120	1.4
	Blend	Liquid	8%	HFC-125	0	3,400	29
			2%	isopro-penyl-1-methyl-cyclo-hexene	0	n/a	n/a
HCFC-124	HCFC	LCG*	$CHClF\text{-}CF_3$		0.022	620	6.1
HCFC-123	HCFC	Liquid	$CHCl_2\text{-}CF_3$		0.02	120	1.4
HFC-236fa	HFC	LCG*	$CF_3CH_2CF_3$		0	9,400	220
HFC-227ea	HFC	LCG*	CF_3CHFCF_3		0	3,500	33

*LCG - Liquefied Compressed Gas
**ODP - Ozone Depletion Potential
***GWP - Global Warming Potential
****CGS – Compressed Gas In Solution
Note 1: Source: IPCC Third Assessment Report (2001)

1.5 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.

1.5.1 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 categorizing its Class A performance.

1.5.2 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.

1.5.3 Electrical Conductivity

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

1.5.4 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.

1.5.5 Range

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

1.5.6 Effectiveness to Weight Ratio

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

1.5.7 Secondary Damage

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

1.6 Selection of an Alternative Streaming Agent

The performance of each alternative is summarized in Table 1-11. The relative importance of each parameter has not been rigorously derived and final selection depends on detailed knowledge of the risk to be protected.

Table 1-11 Portable Fire Extinguisher Capability Comparison

Type	Ordinary Combustibles	Flammable Liquids	Suitable on Energized 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 Fog	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

1.7 Conclusions

Alternative extinguishing agents and technologies are available for nearly all new fire protection applications that previously employed halons. Exceptions are found in certain civil aviation fire protection applications.

1.8 References

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

U.S. Environmental Protection Agency (EPA), "Carbon Dioxide as a Fire Suppressant: Examining the Risks," EPA430-R-00-002, http://www.epa.gov/Ozone/snap/fire/co2/co2report.pdf.