Clean Streaming Agents

by

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Abstract

Although first-generation halon replacements for streaming applications are being commercialized, the search for second-generation replacements is underway. Among, first-generation replacements, HCFC have demonstrated effectiveness but have toxicity concerns and ozone depletion potentials. PFC have demonstrated effectiveness and low toxicity, but have long atmospheric persistence. Therefore, second-generation halon replacement agents with a superior balance of environmental impact, toxicity, and performance are desirable.

The needs of the clean-agent streaming market, the fit of HCFC and PFC into this market, and properties for second-generation agents will be discussed. Also, a new material for a second-generation clean streaming agent will be proposed. The physical properties, extinguishment concentrations, environmental impact, and toxicity suggest that this candidate has a potentially superior balance of desired properties for clean streaming agents than HCFC and PFC.

Introduction

Over one year has passed since the 1994 production ban on halon 1211 (CF_2ClBr). Although significant quantities of halon 1211 exist in installed systems and halon banks, the pressure for end users to make choices on alternative fire protection strategies is mounting.

The pressure to change will redefine the portable (halon 1211) streaming-agent market as a portable clean-agent streaming market. End users gravitating toward this market segment will have determined that they require a clean agent and must choose alternatives based on their individual needs, balancing environmental impact and regulations, performance, and toxicity requirements.

Clean Streaming Agents

Clean extinguishing agents are broadly defined as agents that are electrically non-conductive, volatile, non-corrosive, and leave no residue. These agents are designed to minimize collateral damage to sensitive and high-value equipment. The combination of clean-agent characteristics, effectiveness, and low toxicity made halon 1211 an attractive alternative to water or dry chemicals, even in cases where a clean agent is not required. In the absence of halon 1211, all end users should reevaluate their need for a clean extinguishing agent.

The clean-agent streaming market is faced with the choice between accepting commercially available agents or continuing to use halon 1211 until such a time that more attractive agents are developed. New agent development will take significant time due to chemical development, environmental evaluations, performance evaluation, toxicity testing, code writing, and agent/system listings. Therefore, those with clean-streaming-agent needs must seriously evaluate currently available agents.

The key requirements for clean streaming agents are divided into three categories: environmental impact, performance, and toxicity.

Environmental parameters to consider for clean extinguishing agents include, but are not limited to: atmospheric lifetime, global warming potential, and ozone depletion potential. Long atmospheric persistence alone should not have a deleterious effect on the environment. In contrast, there are effects on the environment from global warming gases and ozone depleting substances (ODS); although, the magnitude of these effects are still open to debate. Proper evaluation of environmental impact must also consider total emission quantities, because significant emissions are required to cause global warming or ozone depletion. In addition to these environmental parameters, clean agent users must consider the regulatory restrictions on alternative agents.

Direct comparison of one streaming agent to another on performance basis is difficult because optimal agent/hardware/technique combination may vary from hazard to hazard. Ultimately, performance based standards must be used, and equally optimized agent/hardware/technique packages should be considered in any comparative evaluation.

In evaluating toxicity for the fire protection industry, both acute and chronic exposures to the agent are of concern. Exposures during actual use and accidental discharge should be considered. Fire fighters may be exposed to high concentrations of agent for short periods under conditions of extreme stress. These concentrations may be as great as the vapor pressure of the material; therefore, acute inhalation hazards must be evaluated. Exposure to lower agent concentrations over extended periods of time is possible; therefore, sub-chronic/chronic hazards levels must be determined. In addition, exposure to toxic byproducts from agent use must be evaluated.

Currently Available Alternatives

Currently there are two commercially available clean-streaming agents that have been extensively evaluated: HCFC-123 including mixtures (e.g. HCFC Blend B, C, and D) and perfluorohexane (FC-5-1-14). Both agents have published results on environmental impact, performance, and toxicity.

HCFC-123

Environmental impact of HCFC-123 has been well studied and the results are summarized in Table 1 (U.S. EPA 1991 and 1994). HCFC-123 has a short atmospheric lifetime and low global warming potential; however, it is an ozone depleting substance (ODS). MacGregor (1994) has evaluated the HCFC environmental impact for the fire protection market; he concluded that the ozone depletion from HCFC in fire protection was insignificant compared *to* that caused by continued recycle and reuse of halons. Under current regulations, production phase-out of HCFC-123 would begin in 2015. In addition, under SNAP guidelines, HCFC-123 (and blends) are approved for use in non-residential streaming applications where other commercially available agents are not as effective for the fire hazard.

Using modified halon 1211 extinguishers, Rochefort et al. (1993) demonstrated that HCFC-123 effectively extinguished class B military fire scenarios but that HCFC-123 not was as effective as halon 1211 (Table 2). Also, those authors demonstrated more rapid extinguishment of several fire scenarios with HCFC-123 than with perfluorohexane (see perfluorohexane comments below). Currently, while it is generally presumed that halocarbons can extinguish class A fires, there are no class A extinguishment data in the literature for HCFC-123. Also, there are no UL-listed portable systems for HCFC-123.

The toxicity of HCFC-123 (Table 3) has been extensively studied (Rusch et al. 1994; Malley et al., 1995). The cardiac sensitization NOAEL and LOAEL (no observed adverse effect level and lowest observed adverse effect level) for HCFC-123 are 1% and 2% respectively. Also, anesthetic-like effects have been observed at concentrations of 0.5% for HCFC-123. Two year chronic studies have shown an increased incidence of benign tumors. Finally, Kibert and Storm (1992) reported that total acid gas (HF + HCl + HBr) generation in the extinguishment of military fire scenarios using HCFC-123 was greater than using halon 1211.

Perfluorohexane

The unique chemical stability of perfluorohexane is evident from its long atmospheric lifetime, 2500-3500 yr. Perfluorocarbons do not react in the troposphere, rather, they disperse to the upper atmosphere where they are destroyed by short-wavelength UV and converted to CO_2 and HF. Given total emission levels, the concentration of these breakdown products is too low to have any environmental impact (Cicerone and Molina, 1991).

The major effect of perfluorohexane's atmospheric persistence is its global warming potential of approximately 5200. This places perfluorohexane in the class of potent greenhouse gases; however, due to relatively-low total emissions, a large impact of PFC on warming is not expected. In contrast, CO_2 has a GWP of 1, but has the largest calculated contribution to global warming due to its enormous volume. Flynn et al. (1994) have evaluated the impact on global warming contribution for all potential perfluorocarbon-ODS replacements. Those authors have determined that all emitted perfluorocarbons would increase surface warming by ~0.001 °C at any time over the atmospheric lifetime of the perfluorocarbon. Leading researchers in the atmospheric sciences have suggested that compounds contributing less than 0.005 °C over 50 yr will have negligible impact on global warming (Ramanathan et al., 1985). Also, perfluorohexane has zero ozone depletion and is not a VOC (volatile organic compound).

Unlike HCFC-123, there are no scheduled production bans on perfluorocarbons. The U.S. EPA has approved the use of perfluorohexane in non-residential streaming applications where other alternatives are not technically feasible due to safety or performance requirements.

The performance of perfluorohexane has been demonstrated in several military fire-fighting scenarios (Pignato et a1.1993). Evaluations at Tyndall Air Force Base and Beaufort MCAS/USN have demonstrated the effectiveness of perfluorohexane. Rochefort et al. (1993) compared HCFC-123, perfluorohexane, and halon 1211. Their work demonstrated that HCFC-123 and perfluorohexane performed well, but neither was as effective as halon 1211. **Also,** their work determined the relative distances from which HCFC-123, perfluorohexane and halon 1211 could extinguish small fires: 0.53, 0.76, and 1 respectively. In addition, those authors concluded that HCFC-123 was faster in extinguishing two of the five fire scenarios; however, perfluorohexane was used in an unmodified halon 1211 extinguisher, while HCFC-123 was used in an extinguisher with 20% greater nitrogen super pressurization and a nozzle with a

117% greater area. Therefore, HCFC-123 system should have delivered a greater mass flow rate to the fire than the perfluorohexane system. Our own work on UL-type heptane pan fires has indicated that higher mass flow rate configurations are more effective. This case illustrates a key difficulty in comparing agent performance: the degree to which agent/hardware/technique systems have been optimized must be considered in making agent comparisons.

Table 1. Environmental impact comparison of halon 1211, HCFC-123, and perfluorohexane (U.S. EPA 1991 and 1994).

Agent	Atm. Lifetime (yr)	GWP (100-yr ITH)	ODP	Regulations
halon 1211	15	NA	3	production ban 1994
HCFC-123	2	90	0.02	production phase-out 2015; other use restrictions
perfluorohexane	3100	5200	0	SNAP restricts use to where other alternatives are not technically feasible due to safety or performance requirements.

Agent	Class A	Class B	UL-Listings
halon 1211	yes	yes	yes
HCFC-123	*no	yes	no
perfluorohexane	**yes	yes	no

Agent	cardiac sens. NOAEL (vol%)	anesthetic effect (vol%)	LC_{50} -rat (vol%)	chronic effects	toxic byproducts (HF, HCl, and HBr in ppm)
halon 1211	0.5 to 1*		10-13*		260 ppm
HCFC-123	1	0.5	3.5	benign tumors	365 ppm
perfluorohexane	>17	none at 30	>30	none known	120 ppm

* range reported in literature (Skaggs and Moore, 1994)

Second Generation Alternatives

The term second generation alternative is frequently used to describe agents that are not commercially available and have superior performance to current halon 1301 or 1211 alternatives. As described above, the key to halon or ODS replacement will be to strike a balance among environmental impact, performance and toxicity. Several companies and government organizations are actively pursing second generation alternatives. At 3M, we are pursuing synthesis and evaluation of new ODS replacements.

Compound A

One of the chemicals which 3M is evaluating is compound A. It is a highly fluorinated compound developed as a potential ODS solvent replacement. Many of the characteristics associated with an ODS solvent replacement, such as non-corrosiveness, volatility, residue free evaporation, and non-flammability are also desirable in a clean streaming agent. Compound A was originally introduced by Klink et al. (1994) as ***liquid A.***

Physical Properties

The physical properties of compound A are shown in Table 4 along with the properties of perfluorohexane for comparison. All properties are practically equivalent to those of perfluorohexane with the exception of the heat of vaporization and dielectric strength. The heat of vaporization for compound A is 42% greater than that of perfluorohexane. This greater heat of evaporation may aid the extinguishing capabilities of compound A. The dielectric strength is 39% less than perfluorohexane but is sufficiently large to qualify as a non-conductive agent. Like perfluorohexane, compound A is a volatile, colorless liquid which is easily handled at room temperature.

Compound A has no closed-cup flash point as determined by ASTM D-3278-89. Some highly-halogenated compounds which exhibit no flash point have been found to form flammable mixtures in air (e.g. HCFC-141b). Such compounds usually require much greater energy ignition sources than hydrocarbons. While definition of flammable limits is important, the ability of a flame to propagate from a fire to a compound A source is of more practical importance. To date, streaming performance data (see below) suggests that formation of these compound A/air/water flammable mixtures is not of practical significance in fire extinguishment.

Table 4. Comparison of physical properties of compound A and perfluorohexane.

Property @23 C.	COMPOUND A	perfluorohexane
boiling point (°C)	60	56
vapor pressure (psia)	3.8	4.5
density (g/cm^3)	1.50	1.68
viscosity (cs)	0.4	0.4
heat of vaporization (cal/g)	30	21
flash point	none	none
dielectric strength (kV)	35	57
surface tension (dynes/cm)	13.6	12.0
specific heat (gas, cal/g/K)*	0.20	0.19
specific heat (liquid, cal/g/K)	0.28	0.25

Flammability limit studies on compound A/air mixtures have been initiated in a spherical 10-liter bomb. Results, to date, are summarized in Table 5. For comparison, data for HCFC-141b is shown; HCFC-141b is known to form flammable mixtures in air under conditions of high ignition energy. The ~100-J ignition source was a 10-in-long, coiled, tungsten wire "exploded" by a DC surge. All tests were run at 100°C and a total pressure of 1.2 ± 0.4 psig.

The 10-liter bomb was capable of igniting HCFC-141b/air mixtures. Under equivalent conditions, compound A did form a flammable mixture; however, introduction of water vapors resulted in the formation of flammable mixtures. Increases in the flammability limits in moist air for highly halogenated compounds has been recently noted by Heinonen et al (1994).

Table 5. Flammability of compound A and HCFC-141b in air and air/water mixtures.

Test Compound	Compound vol%	H_2O vol%	ignition energy (J)	ignition
HCFC-141b	9.1	0	111	yes
Compound A	6.0	3.9	144	yes
Compound A	6.1	2.1	123	no

Environmental properties

The atmospheric lifetime and global warming potential for compound A are greatly-reduced compared to perfluorohexane (Table 6). The atmospheric lifetime of compound A has been determined by its hydroxyl reactivity relative to methane at 298 K. Literature values used to determine the atmospheric lifetime of compound A are the methane-hydroxyl rate constant,

6.5×10^{-15} cm^3/s (Vaghjiani and Ravishankara 1991) and the atmospheric lifetime for methane, 12 yr (Prinn et al., 1991). The global warming potential (relative to carbon dioxide over a 100-year-integrated time horizon) calculations utilized the atmospheric lifetime and the measured IR cross-section. Compound A's ozone depletion potential is zero.

Property	compound A	perfluorohexane
Atmospheric lifetime (yr)	5.5	3100
GWP (CO_2 lb equiv.)	<500	5200
ODP	0	0

Agent	Micro-cup burner (vol%)	heptane-cup burner (vol%)
compound A	6.1	
C_4F_{10}	5.2	5.0-5.9
C_6F_{14}	4.1	4.1-4.4
halon 1301	3.0	2.9-3.5

run on 72 ft^2 pan fires. The test scenario was similar to those run at Beaufort MCAS/UNS to evaluate perfluorohexane (Pignato et al. 1993). The test pan was 12 ft X 6 ft X *8* in., filled with 7 in. of water and ***0.25*** in. of jet-A fuel. All fires were run with a minimum 30-s preburn. Typical military-type extinguishers were charged with agent and pressurized with nitrogen. Agent was directed using typical halon nozzles and hosing.

The results of these tests are summarized in Table ***8.*** Perfluorohexane was used as a control for comparison. The performance of perfluorohexane demonstrated in this test is consistent the results obtained at Beaufort MCAS/USN (Pignato et al. 1993).

These are the first tests performed with compound A. The first test did not extinguish the pan; however, the front edge of the fire was broken, and the fire was pushed to the rear of the pan. The extinguisher pressure was increased in the second test. Again, the front edge of the fire was broken, and the fire was pushed to the rear of the pan. In the third test, the nozzle diameter was increased, and the pan was successfully extinguished.

These tests demonstrate the ability of compound A to extinguish class **B** fires. Optimum technique and system configuration may differ from those of perfluorohexane or halon 1211.

Table **8.** Fire tests on 72 ft^2 jet-A fuel fires using perfluorohexane and compound **A.**

perfluorohexane	9.9
perfluorohexane	11.3
compound A	control but no extinguishment
compound A	control but no extinguishment
compound A	12.5

Toxicity

The toxicity results to date are summarized in Table 9. No effects were observed at 1 vol%-in-air, 4-hr exposure, and the LC_{50} is greater than **10** vol% in air, 4-hr exposure. Compound A is practically non-toxic by ingestion and shows no significant skin or eye irritation.

Table 9. Toxicity results for compound **A.**

Test	Result
Inhalation: LC_{50}-rat @ 4 hr	>10%
Oral Toxicity (LD_{50}-rat)	> 5 g/kg-body weight
Ocular irritation	no significant irritation
Skin Irritation	no significant irritation

Compound A can be manufactured using 3M's existing electrochemical fluorination process capabilities. Therefore, test quantities of compound A may be available in 1996.

Conclusions

HCFC-123 and its blends have demonstrated performance; however, their toxicity and ozone depletion potential will limit their use as a halon 1211 replacement. Perfluorohexane has demonstrated performance as a halon 1211 replacement in certain applications; however, regulatory restrictions due to its atmospheric lifetime will limit its use to applications requiring its safety and/or performance.

Considering the current state of the clean streaming agent market, there is a need for an agent that has a better balance of environmental impact, performance, and toxicity. One of several materials 3M is evaluating as a halon replacement, compound A, shows promise as a streaming agent. Its physical properties resemble perfluorohexane. It has a short atmospheric lifetime, low global warming potential, and is not an ozone depleting substance. Compound A has demonstrated the ability to extinguish military-type class B fires. Also, its acute toxicity is low. Investigation of compound A and other materials as halon replacements is continuing at 3M; however, development of compound A or any other new materials as an extinguishing agent will not be complete until full performance qualification, toxicity testing, code writing, and agent/system listings.

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