THE EVALUATION OF BROMOTRIFLUOROPROPENE AS A HALON 1211 REPLACEMENT

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ABSTRACT

For several years the Advanced Agent Working Group has been investigating bromofluoroalkenes as halon replacements. Being chemically-acting, they offer potential drop-in equivalency. One of the leading candidate agents is bromotrifluoropropene, (BTP, $CF_3CBr{=}CH_2$, AAWG Code #873). It was hoped that this agent could be a suitable replacement for halon 1301, but its cardiotoxic profile, coupled with salient physical properties, mean that it is actually more suited to streaming applications, such as portable extinguishers and wheeled units, where halon 1211 and its replacements are currently used extensively.

The paper will briefly review past work by the AAWG, and then focus on the recent work carried out by Kidde Research. This will cover results from small-scale Class A testing, decomposition product analysis, and assessment of the streaming potential of the agent as a replacement for halon 1211.

INTRODUCTION

The following organisations participate in the AAWG:

US-based: BP Exploration (Alaska) Inc. - on behalf of the Alaska North Slope Oil & Gas Field Owners, the US Army, Navy and Airforce, the US EPA, HARC, NIST, NASA, NMERI and agent manufacturers such as DuPont and American Pacific.

UK-based: The UK MoD, QinetiQ (formerly the UK Defence Evaluation and Research Agency) and Kidde plc.

There are 4 progress meetings per year, usually with the organisations from the UK participating *via* videoconference. The aim of the AAWG may be stated as “finding a drop-in halon 1301 replacement”. It is generally accepted that this implies that the replacement agent will need to be chemically-acting, *i.e*. it must extinguish fires *via* the same catalytic radical removal processes that halon 1301 does. In addition, the agent must have acceptable environmental properties (ODP, GWP), physical properties (*i.e.* sufficiently volatile), and toxicological properties (*i.e*. cardiotoxic NoAEL > design concentration).

The approach was to select candidate molecules that contained both bromine for chemical fire suppression activity and some additional functional group to promote tropospheric degradation, which should result in a short atmospheric lifetime, effectively solving environmental concerns.

The following classes of compounds were included for an initial evaluation: alkenes, alcohols, carbonyl compounds, ethers, amines and aromatics. Several likely candidates from each class were included to generate a list of 24 compounds. Following toxicological screening *via* Quantitative Structural Activity Relationship programmes for both acute and chronic toxicity, this list was reduced to 8 compounds as shown in Table 1.

Table 1: AAWG Downselect Recommendations

Code	Formula	Name
Alkenes		
#872	$CBrF_2CH{=}CH_2$	3-bromo-3,3-difluoropropene
#903	$CBrF_2CF_2CH{=}CH_2$	4-bromo-3,3,4,4-tetrafluorobutene
Alcohols		
#718	$CBrF_2CH_2OH$	2-bromo-2,2-difluoroethanol
Carbonyl Compounds		
#1054	$CBrF_2CH_2C(O)H$	3-bromo-3,3-difluoropropanal
#1056	$CBrF_2CH_2C(O)OCH_3$	methyl 3-bromo-3,3-difluoropropanoate
Aromatics		
#808	$C_6BrF_4CF_3$	1-bromo-3,4,5,6-tetrafluoro-2-(trifluoromethyl)benzene
#953		1-bromo-2,4,5,6-tetrafluoro-3-(trifluoromethyl)benzene
#954		1-bromo-2,3,5,6-tetrafluoro-4-(trifluoromethyl)benzene

- The alkene, #872, was found to be toxic in a preliminary screening test (rats, whole body exposure for 30 minutes at 5 vol%). Seven out of the ten rats died either during the exposure period or within the following two hours [1]. Therefore this compound was eliminated.
- The alcohol, #718, proved to be flammable.

- Of the carbonyl compounds, the aldehyde, #1054, proved to be fundamentally unstable and could not be isolated. The ester, #1056, was very involatile with a vapour pressure far below that necessary to be a flooding agent [2].
- The three aromatic compounds were similarly of very low volatility, and these were also eliminated.

At this point only compound #903 remained, which had not been tested for toxicity, and was of questionable volatility. Therefore further alkenes were added to the list including agent #873, 2-bromo-3,3,3-trifluoropropene (BTP). This compound appeared much more promising, and the remainder of this paper will focus on this compound.

PHYSICAL PROPERTIES OF BTP

Table 2 below shows the physical properties of BTP, and compares them with those of halon 1301 and halon 1211.

Table 2: Physical properties of BTP

Name	Halon 1301	Halon 1211	BTP
Chemical Formula	CF_3Br	CF_2BrCl	$CF_3CBr{=}CH_2$
ODP	10	3	0.0037[A]
Atmospheric Lifetime (years)	65	11	0.011[B]
Molecular Weight	148.90	165.36	174.95
Boiling Point (°C)	-57.8	-4	34
Vapour Pressure (bar(a) at 25°C)	16.0	2.8	0.74
Liquid Density ($g.cm^{-3}$ at 25°C)	1.54	1.8	1.65

[A] Data supplied to AAWG by EPA [3]

[B] Data supplied to AAWG by NIST [4]

On examining the physical properties it can be readily appreciated that BTP is much more likely to be a viable halon 1211 replacement than a halon 1301 replacement. Its atmospheric lifetime has been calculated by NIST to be 3-5 days, making it much more environmentally acceptable than either halon 1211 or 1301.

TOXICITY TESTING

The commercial success or failure of novel extinguishing agents depends as much, if not more, on the agent's toxicity as on its fire extinguishing properties. So far, limited toxicity testing has been carried out on BTP. This is summarised below in Table 3.

Table 3: Toxicity Testing Completed

Item	Comments
AMES	Mutagenic test. Complete. No mutagenic effects noted [5].
Human Lymphocyte (Chromosomal Aberration)	Mutagenic test. Complete. No mutagenic effects noted [6].
Preliminary Limit Test (5% concentration for 30 min)	This is a low concentration test to determine if chemical is lethal. Complete. Some potential anaesthetic effects noted [1].
Cardiotoxic Dog Inhalation	Complete NoAEL 0.5% LoAEL 1.0% [7]

Thus it can be seen that BTP is not suitable for total flooding in occupied areas, as the cardiotoxic NoAEL is below the cup burner concentration. However, the toxicological requirements for streaming agents are less stringent. In fact the NoAEL and LoAEL values for halon 1211 are also 0.5 and 1.0 vol% respectively. Thus BTP would appear to be viable as a streaming agent from a toxicological viewpoint.

In addition, further toxicity testing, possibly a 90-day subchronic test, would be required. This will allow assessment of any chronic effects, to protect workers involved in prolonged or repeated exposure to the agent, for example those involved in manufacture or distribution.

FIRE TESTING RESULTS

As the AAWG are searching for a total flood agent, the fire testing carried out was centred in this area, and small scale flooding tests were carried out. Also, as BTP is currently only available *via* laboratory-scale custom synthesis, any large scale streaming tests would be prohibitively expensive. Nevertheless some real-scale tests using small hand extinguishers have been carried out to assess the agent's potential as a streaming agent.

CUP BURNER MEASUREMENTS

The Kidde Research cup burner has been described previously [8]. One of the features of this particular cup burner is the ability to measure agents of reduced volatility, such as chlorobromomethane (CB, halon 1011; b.p. 67°C) and the AAWG agents. Another feature is the ability to control the fuel temperature at the point of extinction. Previous experience indicates that for *n*-heptane as the fuel, a temperature of *ca*. 50°C requires the highest agent concentration. Therefore this temperature is selected to generate conservative extinguishing data. Values for several extinguishing agents are included in Table 4 below.

Table 4: Cup Burner Results

Agent	Fuel Temperature (°C)	Extinguishing Concentration (Vol%)
Halon 1301	57	3.6 ± 0.1
Halon 1011	50	4.1 ± 0.2
Bromotrifluoropropene	55	4.6 ± 0.1
HFC-227ea	50	6.8 ± 0.1

All values obtained with an airflow of 30 L/min.

FID EXTINGUISHING CONCENTRATION

Researchers at QinetiQ (formerly the UK Defence Evaluation and Research Agency, DERA) have developed a novel agent screening apparatus. It consists of a gas chromatograph flame ionisation detector (FID) which has been modified to permit measurement of extinguishing concentrations of halon replacement agents [9]. The apparatus permits rapid determination of extinguishing concentrations and requires only a few grams of agent, making it ideal for screening novel agents.

As members of the AAWG, QinetiQ have evaluated several of the agents; relevant results are included in Table 5 below [10].

Table 5: FID Extinguishing Results

Agent	FID Extinguishing concentration (Vol%)
Halon 1301	2.9±0.1
Halon 1011	3.6±0.2
Bromotrifluoropropene	4.5

SMALL SCALE CLASS A FIRE TESTING

A small-scale Class A wood crib (referred to as the “Mini-Crib”) for investigating the behaviour of aqueous agents was devised by Kidde Research and presented at a previous Halon Options Conference [11]. The crib has since been modified to allow testing with gaseous agents. The modified crib consists of sixteen members (65 mm x 10 mm x 12 mm) arranged in four bundles of four, as depicted below. A K-type thermocouple (T/C) was used to gauge the core crib temperature.

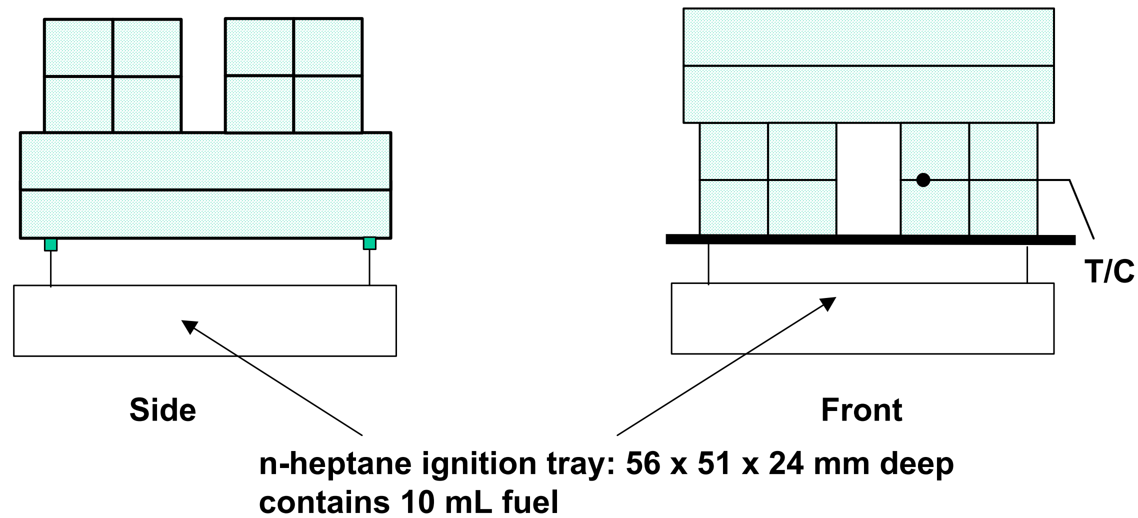

Figure 1: Mini-Crib used for Small Scale Class A Tests

The Mini-Crib was positioned in a 287 L test chamber as shown in Figure 2, which indicates the relative positions of the nozzle, crib *etc.*

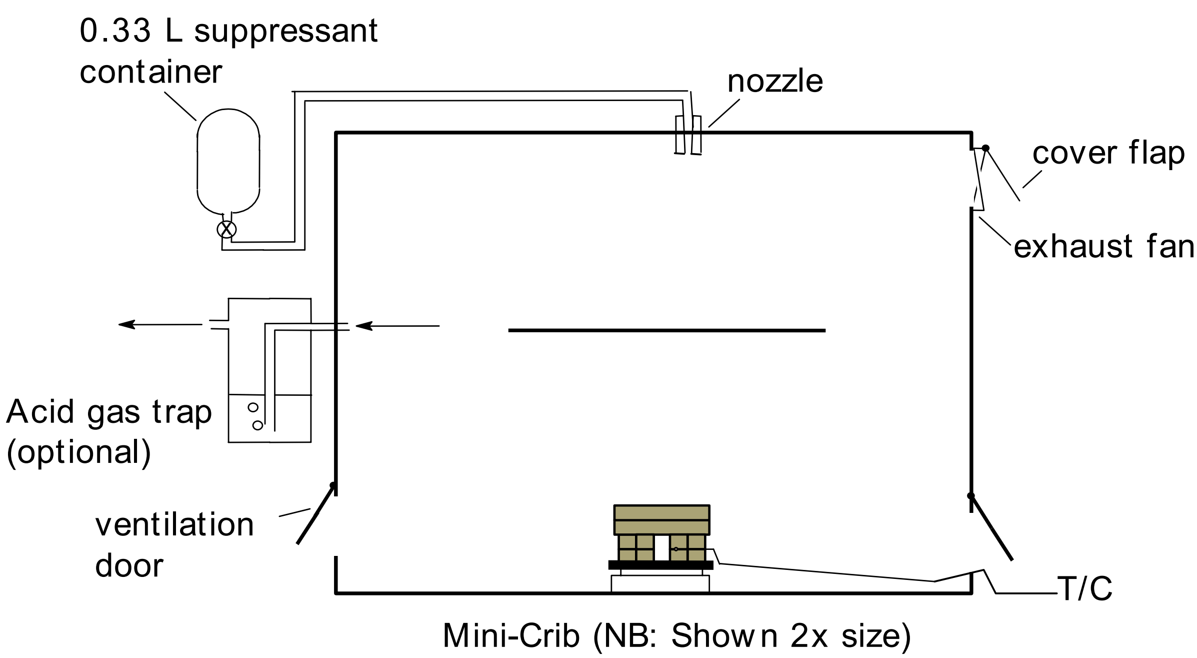

Figure 2: 287 L Test Chamber

The agent was stored in a 0.33 L stainless steel reservoir, and released manually *via* a ¼" ball valve. Stainless steel tubing (¼") transferred the agent to the nozzle (Lurmark TN series; 1.0 mm orifice). All agents were pressurised with dry nitrogen to 10 bar(g). This arrangement gave discharge times between 5 and 15 s, depending on the amount of agent being deployed. The mass of agent deployed was converted into a gas volume% concentration, using values of specific volume from the following standards:

Agent	Standard
Halon 1211	NFPA 12B
FM-200	NFPA 2001
BTP	Ideal gas behaviour assumed, with (C/100-C) correction term

A pre-burn period of 4 minutes (partly under forced ventilation) was found to give reproducible burning behaviour. The mass of agent in the 0.33 L vessel was varied and the fire-out time noted. Figure 3 below indicates typical results for the agents tested: halon 1211, BTP and HFC-227ea. The form of the relationship between agent mass and fire-out time has been seen previously in small-scale fire chambers [12]. Essentially, if insufficient agent is deployed, a long fire-out time is observed; the fire being eventually extinguished by a combination of deployed agent and oxygen depletion.

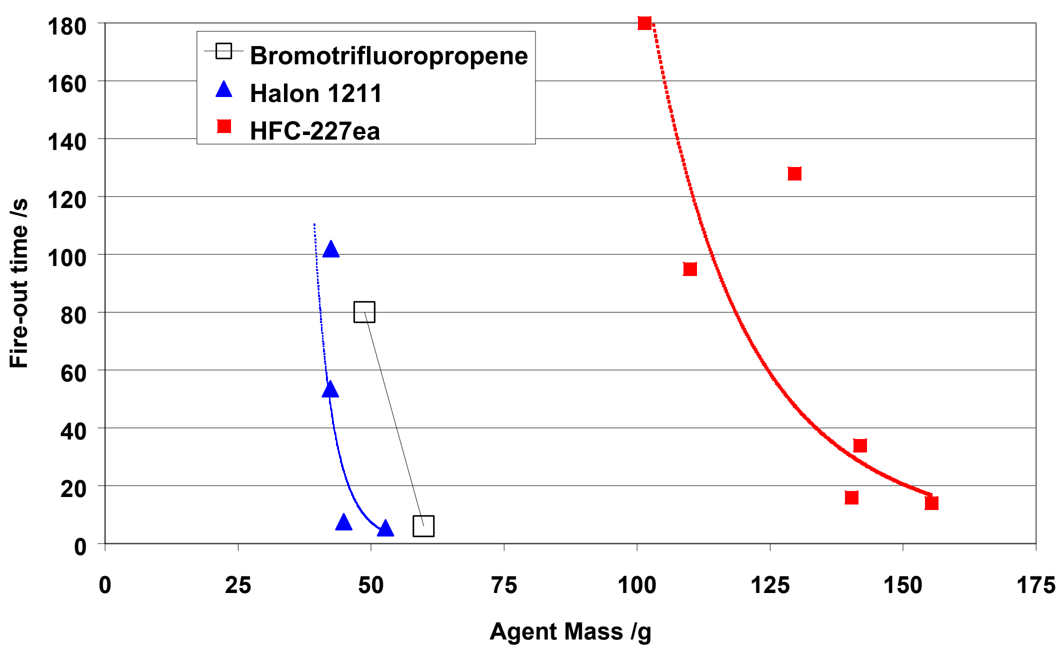

Figure 3: Class A Fire Test Results

It can readily be appreciated that BTP is very close in mass terms to halon 1211. Both of these agents, being bromine-containing, and therefore chemically-acting, are much more efficient than an agent such as HFC-227ea, which essentially relies on heat capacity effects.

SMALL SCALE CLASS B FIRE TESTING

The Kidde Research small-scale test chamber and protocol for class B fires has been described extensively previously [12,13]. Typical results are included in Figure 4 below.

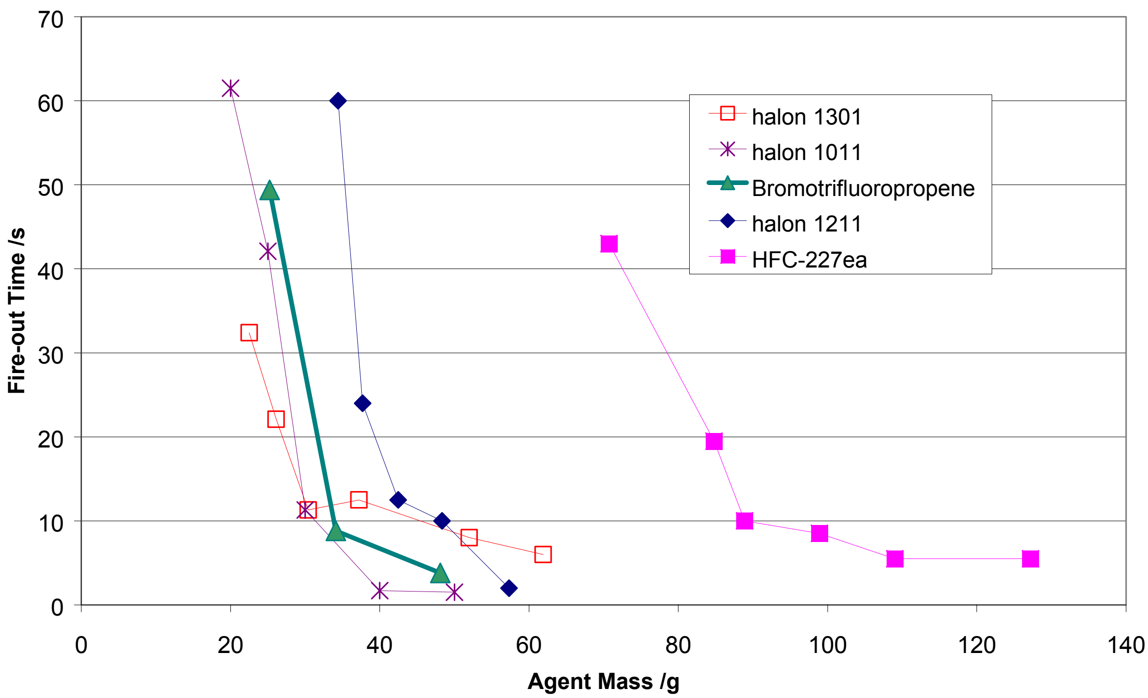

Figure 4: Class B Fire Test Results

Again, it can bee seen that the bromine-containing (and therefore chemically-acting) agents, including BTP are much more efficient than agents that do not contain bromine, such as HFCs.

FULL SCALE STREAMING TEST RESULTS

Given that the agent looked promising from laboratory scale tests, some full scale hand extinguisher tests were carried out at UL Canada. The extinguisher was a 2.5 pound Kidde halon 1211 unit, as used in aircraft cabins. The fire was a UL 5B (square pan, 1.08 m × 1.08 m × 0.30 m deep, filled with 6 inches (0.15 m) of water and 2 inches (0.05 m) of *n*-heptane fuel). The extinguisher was charged with 3.5 pounds (1.59 kg) BTP. The only modification to the extinguisher was that the standard nozzle orifice was increased to permit a higher mass flow rate, thus keeping the overall extinguisher discharge time around 9 s. The UL 5B fire was successfully extinguished using this extinguisher, in 5.2 s, with less than 2.5 pounds of BTP being discharged. This proves that the agent is very effective, and can be viewed as a drop-in replacement for halon 1211.

Although attempts to reduce the mass of agent did not result in fire extinguishment, very good initial fire knock-down was achieved. It is believed that the non-optimised nozzle was producing a relatively narrow discharge cone angle with BTP, due to its lower volatility compared to halon 1211. These results give confidence that further testing with a more appropriate nozzle would achieve the desired rating with a mass of agent equal or close to that of halon 1211.

SUMMARY & CONCLUSIONS

BTP is a drop-in replacement for halon 1211. Like halon 1211, it is a chemically-acting fire extinguishant, and both agent have similar toxicological profiles. Unlike halon 1211, BTP has a significantly reduced environmental impact, by virtue of its being tropodegradable.

BTP has been shown to be equivalent to halon 1211 in small-scale hand extinguisher tests, but it is believed that it could also replace halon 1211 in other applications, for example wheeled units. It could also be used for total flooding in non-occupied areas, such as aircraft cargo bays, and possibly engine nacelles.

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