EVALUATION OF ADVANCED AGENT WORKING GROUP AGENTS BY KIDDE

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INTRODUCTION

Since the production ban of halons, following the Montreal Protocol, a number of halon replacement agents have been available. For most applications, these agents are perfectly acceptable, and have found widespread use. However, there are some applications, where the increased space and weight requirements mean that these so-called "first generation" replacements are not acceptable. For some years recycled halon has been used, but there are concerns that the "Halon Bank" is becoming depleted in the US. This has highlighted the need for a chemically acting, drop-in replacement for Halon 1301.

For the last 5 years the Advanced Agent Working Group (AAWG) has been funding research into "second generation" halon alternatives. One avenue has been that of tropodegradable bromocarbons, which retain the chemical fire suppression properties of halon, but incorporate functional groups that promote rapid atmospheric degradation, thus minimising both ozone depletion and global warming.

This paper presents recent work carried out by Kidde as part of AAWG activities. Full-scale ISO cup-burner measurements and small-scale total-flooding experiments are described, including analysis of decomposition products and comparison with first generation halon replacement agents. In addition, small-scale inerting tests have been carried out at the Fenwal Safety Systems, Combustion Research Center, Holliston, MA. Three candidate tropodegradable bromocarbon molecules were short-listed for detailed study by the AAWG: 2-bromo-3,3,3-trifluoro-1-propene (BTP); 4-bromo-3,3,4,4-tetrafluoro-1-butene (BTFB); and 2-bromo-3,3,4,4,4-pentafluoro-1-butene (BPFB). The AAWG supplied all samples of these agents.

PHYSICAL PROPERTY DETERMINATION

VAPOUR PRESSURE / TEMPERATURE CURVES

RATIONALE : The introduction of groups or moieties that promote tropospheric degradation inevitably increases molecular weight and decreases volatility [1]. Therefore, assessment of vapour pressure/temperature (v.p./T) characteristics, together with an appreciation of the temperature requirements of the specific fire protection application, is an essential part of the screening process for new agents. Many early candidate agents were dropped from the AAWG programme purely due to their low volatilities. The usual quoted measure of an agent's volatility is its boiling point. However, this serves only as a guide; the real determinant of whether an agent can be used for total flooding is that its vapour pressure (expressed in atm) must exceed its extinguishing concentration (expressed as a mole fraction) [2].

APPARATUS : Kidde Research has developed a simple apparatus for measuring v.p./T characteristics as a screening tool for candidate agents. This is shown schematically in Figure 1. Pamasols (DH Industries;* part no. P200/1) are heavy walled glass tubes that can withstand pressures in excess of 10 bar(g). This makes them ideal for this kind of application, as visual checking that liquid agent is still present is essential. The Pamasol lid had a feed-through for a K-type thermocouple; the tip of which was located in the liquid agent. The Pamasol lid also had a fitting for a type 4045-A5 Kistler piezo-resistive transducer that was coupled to a type 4601 bridge amplifier for pressure measurements.

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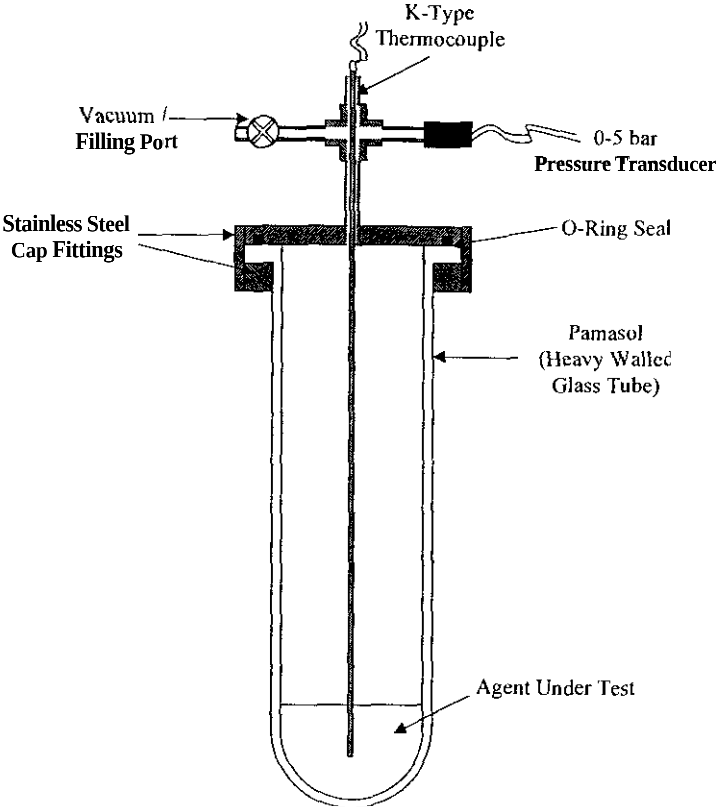

Figure 1. Apparatus for vapour pressure versus temperature measurements.

PROCEDURE : Approximately 10-20 mL of the agent were placed in the Pamasol, which was then assembled and sealed. The Pamasol was then immersed in liquid nitrogen to freeze the agent and the residual air was evacuated. This process was repeated twice to remove **any** air or nitrogen dissolved in the agent. The apparatus was then weighed to 0.01 g. The Pamasol was cooled again in liquid nitrogen, lagged with cotton wool, and allowed to slowly warm up to room temperature. The temperature of the agent inside and the vapour pressure were then recorded. Heating above room temperature was achieved by immersing the whole apparatus in a water bath that was slowly heated. A corresponding cooling curve was **also** obtained, to check for hysteresis due to thermal lag. Finally, the weight was checked to ensure no leakage had occurred.

RESULTS : A graph **of** the v.p./T curves **for** the three candidate agents is given in Figure 2. It can be seen that the boiling points of the agents (i.e., v.P. at 1.00 atm or 1.01325 bar(a)) are as follows: BTP 34 °C, BTFB *65* °C, and BPFB 59 °C. The relative boiling points are expected; the propene molecule (BTP) has a lower boiling point than the butene molecules and, of the butene molecules, the one containing the most fluorine atoms (BPFB) has a lower boiling point [1].

DENSITIES

The density of BTFB was determined using a 4-figure balance and a 10 mL volumetric flask. BTFP has a liquid density of 1.60 g/mL at 23 °C. Owing to the proximity of BTP's boiling point to room temperature, its density was measured **by** weighing 80 mL in a Pamasol (see above) using a 2-figure balance. BTP has a liquid density of 1.65 g/mL at 22 °C.

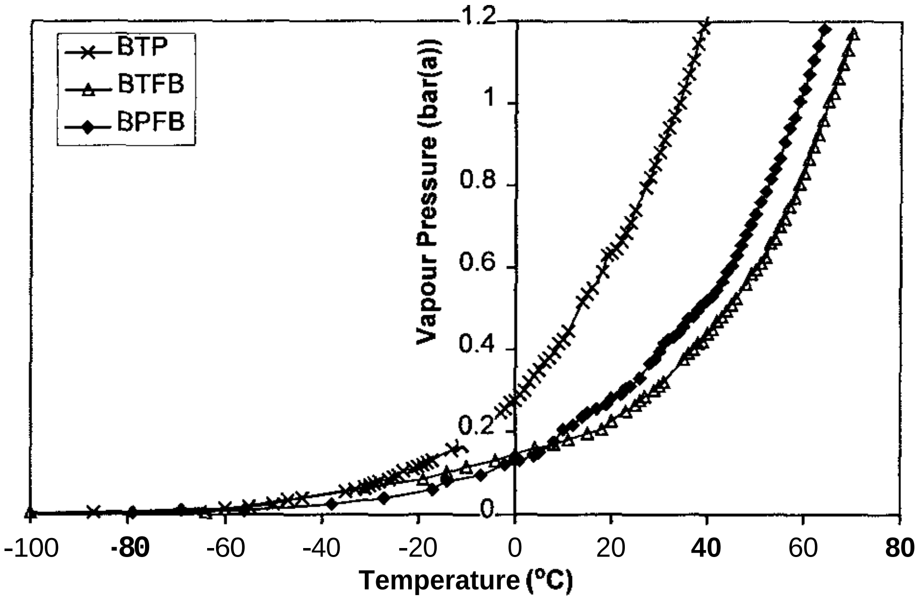

Figure 2. Dependence of the vapour pressure on temperature for the three agents tested.

FIRE SUPPRESSION TESTING

CUP-BURNER TESTING

APPARATUS: The Kidde Research cup burner has been described previously [3]. The description included technical drawings of the design, and details of the construction materials, instrumentation, and method of operation. The AAWG agents are relatively involatile and require a special method of delivery; the apparatus used is shown in Figure 3. Extinguishing concentrations were measured by FTIR spectroscopy of grab samples collected in Tedlar bags immediately after extinguishment of the flame.

METHOD OF FTIR CALIBRATION: A Mattson Research Series FTIR spectrometer with a Perkin Elmer 20 m variable path length gas cell was used. Calibration was achieved by direct liquid injection of BTFB into an air stream entering the previously evacuated gas cell. With BTP this method would not have been reliable because the boiling point of this agent is too close to room temperature. Therefore, syringe samples were taken from the vapour headspace above liquid BTP at known temperature and injected into the gas cell air feed. The agent concentration was calculated from the v.p./T data (Figure 2).

METHOD OF AGENT DELIVERY: Agent (about 250 g) was charged into a pressure vessel (0.3 L), which was fitted with a pressure gauge and metering valve (Figure 3). The whole assembly was immersed in a thermostatically controlled water bath. Suitable volatility was achieved for BTP when the water bath was regulated at 50 °C; BTFB required a water temperature of 95 °C.

EXPERIMENTAL PARAMETERS: Previous measurements with the Kidde Research cup burner show that the extinguishing concentration of halocarbon agents such as HFC-227ea do not vary significantly with air flows from about 20 to 50 L/min (e.g., Grigg [3]). For this reason, and because the AAWG agents were in limited supply, an air flow of 30 L/min was used for all measurements in the current study. Air flows above 30 L/min would require more agent. Previous measurements with n-heptane fuel have also shown that all agents (halocarbons and inert gases) have a maximum extinguishing concentration with a fuel temperature, at the point of extinguishment, of 50 °C. This fuel temperature was used throughout this study.

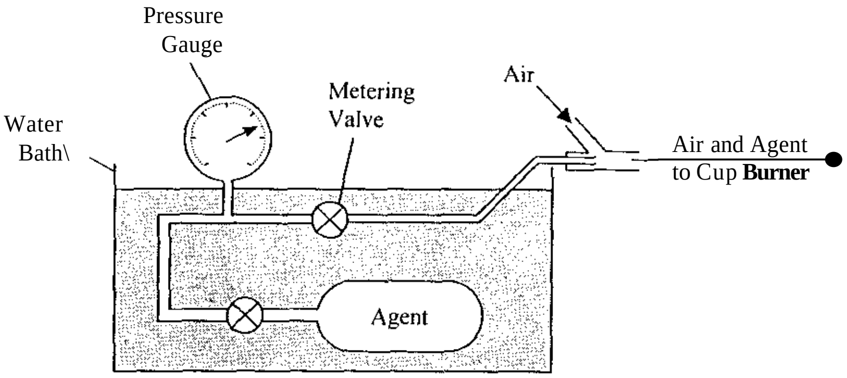

Figure 3. Apparatus for the delivery of low volatility agents into the cup burner.

RESULTS: The extinguishing concentrations of BTP and BPFP, together with those of HFC-227ea, Halon 1011, and carbon dioxide for comparison, are given in Table 1. These measurements were all conducted under identical conditions; fuel temperature 50 °C, air flow 30 L/min.

TABLE 1. KIDDE RESEARCH CUP-BURNER EXTINGUISHING CONCENTRATIONS OF VARIOUS AGENTS.

Agent	Extinguishing Concentration (volume%)
BTP	4.7 ± 0.2
BTFB	5.0 ± 0.3
HFC-227ea	**6.8** ± 0.1
Halon 1011	**4.1** ± 0.2
Carbon Dioxide	22.7 ± 0.5

Note: **Fuel** = n-heptane **at** 50 °C, **Air** Flow = 30 Llmin

SMALL-SCALE TOTAL-FLOOD TESTING

APPARATUS : BTP was tested in the Kidde Research small-scale test chamber. This chamber has been described in detail previously [4]. It has a volume of 200 L, and the fire threats are three **small** pans containing n-heptane floated on water. The main fire (n-heptane volume 30 mL and diameter 70 mm) was positioned in the centre of the base of the chamber. Two satellite fires (n-heptane volume 1 mL and diameter 20 mm) were positioned at the bottom right front comer and the top left rear comer. This gave a value of 7.3 kWm^{-3} for the fire size to chamber volume parameter (FSRV). All fires were obscured with baffles. Acid gases were determined by trapping in water and subsequent analysis using fluoride or bromide ion selective electrodes.

PROCEDURE: The test methodology **has** been described previously [4]

RESULTS: **A** convenient way of displaying results **from** the 200 L chamber is by plotting the extinguishment time versus the agent concentration. The results for BFP, along with those **for** HFC-227ea and Halon 1301 are given in Figure 4. The results in this figure show that when, for example, a concentration above about 5.8 vol% of HFC-227ea is discharged, **a** minimum extinguishment time of 8 to 10 sec is observed. If a lower concentration of this agent is discharged, the extinguishment time is increased. This is because, when insufficient agent is supplied to the chamber, extinction occurs through a combination of oxygen depletion caused by continued burning of the fire and the raised heat capacity due to the agent and products of combustion. This gives a "break point" for HFC-227ea of about 5.8 vol%. The "break points" for both Halon 1301 and BTP are about 2.4 vol%.

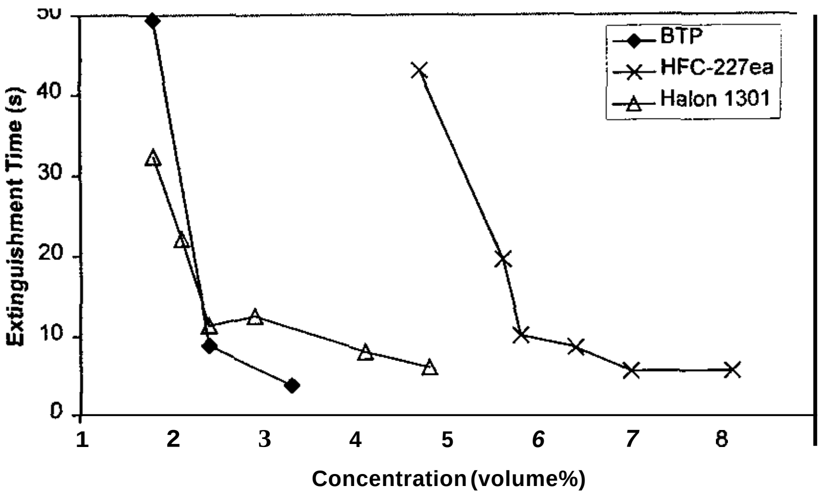

Figure **4.** Comparison of the extinguishing efficiencies of BTP, HFC-227ea, and Halon 1301.

Tests of many agents in the 200 **L** chamber show that the break point value is always below the cup-burner extinguishing concentration because of inhomogeneous agent distribution; there is a greater agent concentration at lower positions. In fact, the higher the boiling point of the agent the better it performs in the 200 **L** chamber. Therefore, extinguishing concentrations determined in this chamber are not direct indications of cup-burner values but are valuable guides to the fire suppression abilities of the agents.

In addition to producing extinguishing time data, the 200 L test chamber has been designed to allow sampling of the chamber contents for gas analysis. Graphs of acid gas concentration versus time after the beginning of discharge for BTP, HFC-227ea, and Halon 1301 are given in Figures 5 to 7. In general, if the concentration of agent is increased, the concentration of acid gases is reduced. For BTP, a concentration of about 1000 ppm is generated in the 200 L chamber with an agent concentration of 3.3 vol%, about 2000 ppm is generated with **2.4** vol%, and about 6000 ppm is generated with 1.8 vol%. It is possible to compare the concentrations of acid gases generated from BTP with those of other agents if the results compared are from similar ratios of the extinguishing concentration to the cup-burner concentration for **all** agents. The results in Figures 5 to 7 of BTP at 3.3 vol% may be compared with those of HFC-227ea at 5.6 vol% and Halon 1301 at 2.9 vol%. About the same concentrations of HF and HBr were generated from BTP and Halon 1301 at concentrations of 3.3 and 2.9 vol%, respectively. **A** higher concentration of HF was generated by HFC-227ea at ***5.6*** vol%. This has been observed before [4].

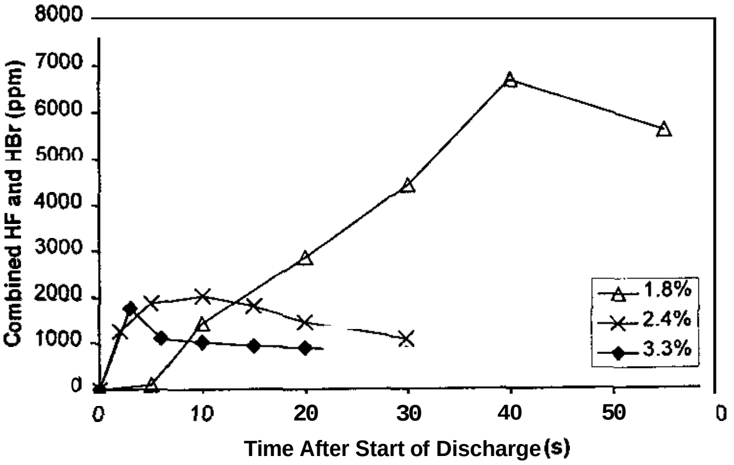

Figure 5. HF concentrations generated during fire tests with BTP (7.3 kWm^{-3} heptane fire in 200 **L** chamber).

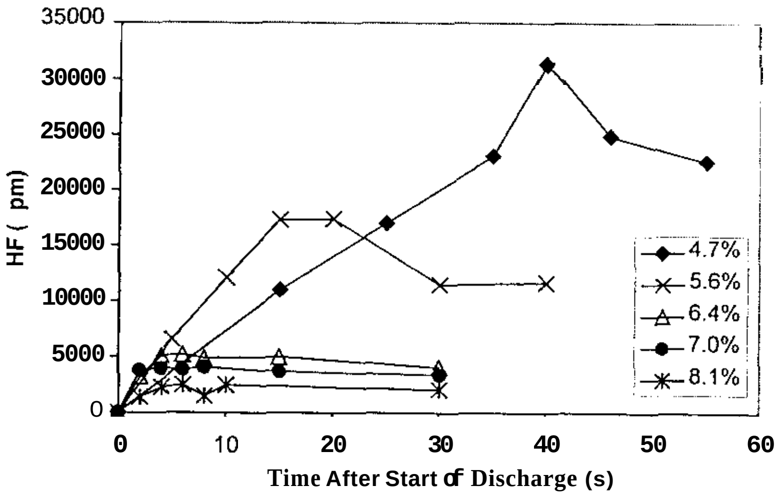

Figure *6*. **HF** concentrations generated during fire tests with HFC-227ea (7.3 kWm^{-3} heptane fire in 200 L chamber).

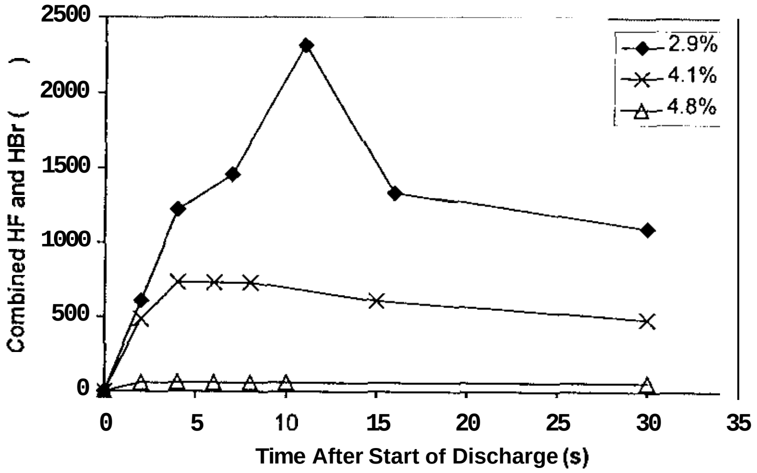

Figure 7. HF concentrations generated during fire tests with Halon 1301 (7.3 kWm^{-3} heptane fire in 200 **L** chamber).

INERTION TESTING

APPARATUS: The 7.8 **L** sphere used for these tests is shown in Figure 8. It is located at the Fenwal Safety Systems Combustion Research Center. The small size of the sphere makes it ideal for screening limited quantities of agent.

PROCEDURE: Owing to the low volatility of the agents, the vessel was heated to the approximate boiling point of the agent in question. The vessel was purged to remove any gases remaining **from** the previous test and then evacuated. The fuel (methane or propane) was introduced up to the partial pressure required. The agent was introduced and its partial pressure was noted. The pressure in the vessel was then adjusted to 1 atm by the introduction of atmospheric air. The vessel was allowed to stand to aid vaporisation of the agent. A spark of energy 10 mJ across a **6** mm gap between carbon electrodes comprised the ignition system. **A** successful test outcome was defined as a pressure rise of less than 7% of the initial pressure, or 1 psi. **A** full description of the procedure may be found in ASTM E 2079-00 [5].

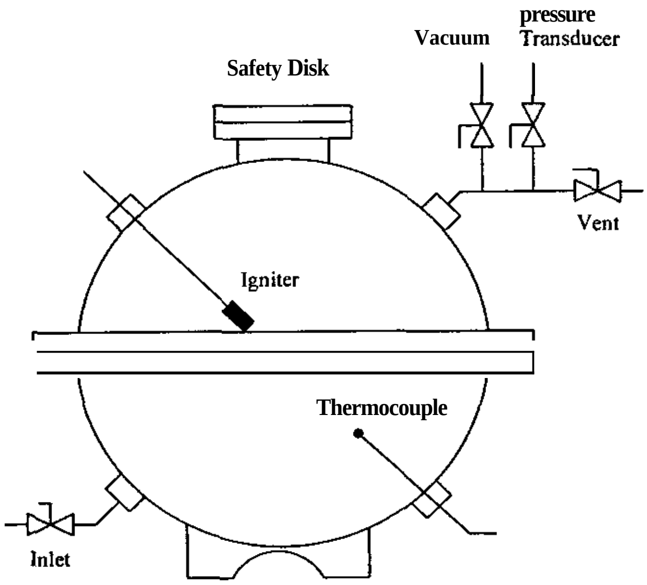

Figure **8.** Apparatus for inerting measurements.

RESULTS: Table 2 gives the results obtained, along with those for Halon 1301 and HFC-227ea for comparison. It can be seen that BTP is of intermediate efficiency between Halon 1301 and HFC-227ea, whereas BTFB is of comparable efficiency to Halon 1301.

TABLE 2. INERTING CONCENTRATIONS,

Agent	Methane Inerting Concentration (vol%)	Propane Inerting Concentration (vol%)
BTP	–7	8.5 ± 0.4
BTFB	–4	6.3 ± 0.4
Halon 1301	4.0 (errors not available)	7.7 (errors not available)
HFC-227ea	8.0 (errors not available)	11.5 (errors not available)

DISCUSSION

EXTINGUISHING EFFECTIVENESS

The AAWG agents contain bromine, and therefore have the potential for chemical fire suppression activity. However, they also contain C-H and C=C moieties, which can be considered as contributing fuel-like properties, and therefore have a detrimental effect on fire suppression ability [6]. This indeed is the case. Figure 9 shows a plot of extinguishing concentration (cup burner, n-heptane) vs. heat capacity.

The heat capacities of the AAWG agents were calculated using Benson Groups [7]. Physically acting agents work by abstracting heat, and therefore, to a first approximation, their extinguishing concentration can be deduced from their heat capacity [8]. Hence, they all fall on or near the line in Figure 9.

Any deviation from this line implies an additional (chemical) fire suppression mechanism. Halons lie well off this line, implying considerable chemical suppression ability. In fact, the chemical contribution for Halon 1301 has been calculated to be –80% [8]. The AAWG compounds lie closer to the "physical suppression" line, presumably reflecting their partial fuel character.

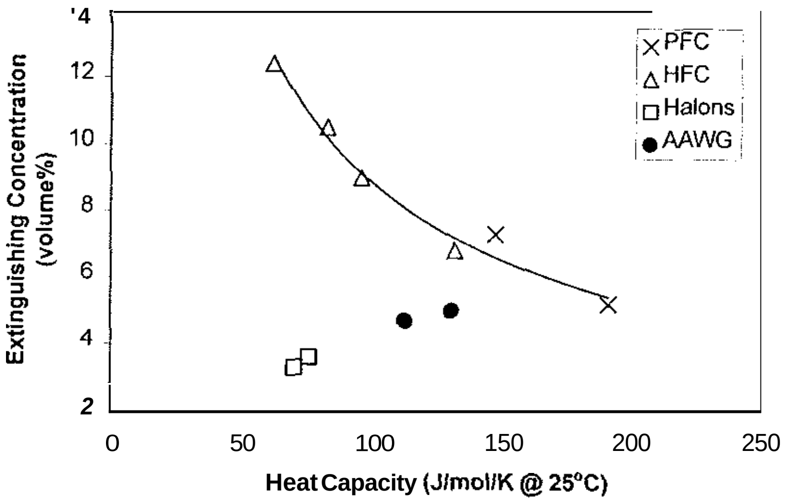

Figure **9.** Extinguishing concentration vs. heat capacity

TEMPERATURE RANGE

Now that the v.p./T and the fire suppression characteristics are known for BTP and BTFB, it is possible to calculate the lower temperature limits to which these agents can be used (see earlier discussion). Theoretical minimum use temperatures are given in Table **3**.

TABLE **3.** THEORETICAL MINIMUM USE TEMPERATURES.

Agent	Cup-Burner Value (vol%)	Minimum Design Concentration (vol%)	Theoretical Minimum Use Temperature ("C)
BTP	**4.7**	5.6*	**-34**
		6.1**	-32
BTFB	5.0	6.0*	**-23**
		6.5**	-21

* Safety **Factor** = 1.2 (NFPA 2001 **Class A)**

** Safety Factor = 1.3 (ISO 14520 and **NFPA** 2001 **Class B).**

These values represent absolute minima; these are the temperatures above which the agent has sufficient vapour pressure to achieve an extinguishing concentration; no account is taken of the speed of vaporisation. This is an area of ongoing research and modelling.

INERTING EFFICIENCY

It is established that inerting is more dependent on physical suppression mechanisms than fire suppression, which is very dependent on chemical suppression mechanisms [9]. The advantages of chemically acting agents are therefore reduced in inerting applications. The results given above show that for BTP, BTFB, Halon **1301,** and **HFC-227ea,** the relative inerting efficiency does not correlate with the cup-burner extinguishing concentrations. The greater heat capacity of the **AAWG** agents (especially BTFB) is **of** benefit for inerting.

CONCLUSIONS

The results are encouraging; the agents are definitely chemically acting, and are more efficient than the physically acting first generation halon replacements. They are, however, less efficient than halons, **as** was predicted previously [1].

Calculations by NIST indicate atmospheric lifetimes of all the AAWG compounds to be in the order of days, so no environmental disadvantages (ODP, GWP) are envisioned.

The physical properties (vapour pressure vs. temperature characteristics) of these agents are not as attractive as those of Halon **1301** for total-flood applications. There will definitely be greater temperature restrictions on these new agents. However, theoretical minimum use temperatures as low as about **-30** °C indicate that these agents are feasible for use in many applications. In addition, both BTP and BTFB have liquid densities greater than Halon **1301,** which allows slightly more efficient storage.

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