

IN SEARCH OF ALTERNATIVE FIRE SUPPRESSANTS

William L. Grosshandler
Building and Fire Research Laboratory
National Institute of Standards and Technology
Gaithersburg, Maryland
U.S.A.

ABSTRACT

The common fire fighting agent halon 1301 (CF_3Br) is among a number of halogenated chemicals that are sufficiently deleterious to stratospheric ozone that their continued production and use has been severely curtailed. Halons had been the agents of choice for numerous fire protection applications because of their inherent ability to inhibit flames at low concentrations with no residue while exhibiting a number of additional strongly positive attributes. The elimination of new production of halon has forced the fire suppression systems manufacturers, the transportation and communications industries, and other large users of these products to search for suitable alternatives. If the alternative chemicals are less efficient suppressants, then new, larger agent storage and delivery components need to be designed. To avoid costly mistakes in choosing replacements for aircraft applications, research has been conducted to determine the performance of different agents in extinguishing aircraft-type fires. This paper describes the major elements of the overall program and the rationale of how an alternative to halon 1301 was chosen for aircraft applications.

BACKGROUND

Up until 1987 little thought was given to the impact on the environment caused by the suppression of unwanted fires. Of primary concern was the immediate protection of the threatened structure and affected personnel, with some concern also expressed about the negative impact of the particulate, organic vapors and NO emitted by the fire on smog and atmospheric visibility. The chronic health effects created by direct, long term exposure to the suppressing agents, or from byproducts of chemical reactions in the environment were ignored.

The recent environmental problems associated with halons have been well publicized. The Montreal Protocol of 1987 identified the common fire fighting agents, halon 1301 (CF_3Br) and halon 1211 (CF_2ClBr), as among a number of halogenated

chemicals that were sufficiently deleterious to stratospheric ozone that their continued production and use required limitation. An amendment to the Protocol caused commercial halon production to cease at the beginning of 1994 (Harrington, 1993).

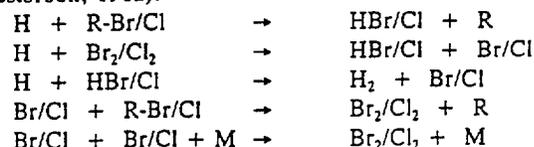
The focus of concern is the change in reactivity of the halon molecule from the lower atmosphere to the upper atmosphere. Hydroxyl radicals react slowly with the bromine atom in the troposphere, and the sunlight is not energetic enough to break the carbon-bromine bond. Therefore a large percentage of the halon molecules are transported to the stratosphere intact. Once there, photodissociation by solar ultraviolet radiation occurs and the liberated bromine atom enters into the following catalytic cycle (World Meteorological Organization, 1989):



Chlorine reacts in an analogous but less aggressive manner because the C-Cl bond is stronger. The net effect of free Br and Cl atoms is the consumption of the shielding stratospheric ozone.

Trifluorobromomethane (CF_3Br) depletes ozone at a rate approximately 15 times that of freon 11 (CFCl_3), which is to say CF_3Br has an ozone depletion potential (ODP) of ≈ 15 . The ODP for CF_2ClBr is ≈ 3 . The maximum value of ODP currently acceptable under the 1990 amendment to the Clean Air Act is 0.2.

Halons are unusually efficient at suppressing combustion because the bromine (and chlorine, to a lesser extent) ties up the hydrogen atoms which are critical to the chain branching reactions. This is thought to occur through the following kinetic scheme (Westbrook, 1982):



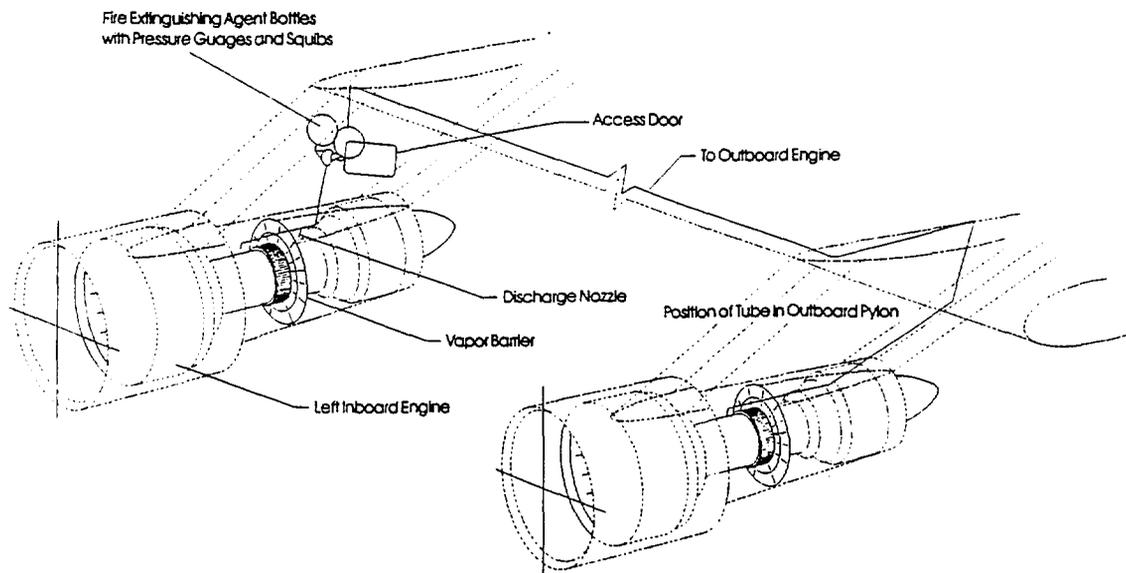


Figure 1. Schematic of wing-mounted nacelle and fire extinguishing system (courtesy of M.L. Kolleck, Booz-Allen & Hamilton, Inc.).

R represents a hydrocarbon fragment and M is any third body. Additional inhibition is provided through bromine reactions which reduce the O and OH radical pool.

The physical characteristics of CF_3Br are also somewhat unique. This compound is a liquid at room temperature and 1.61 MPa, has a high liquid density, and remains stable for years, all attributes important for satisfactory storage. The electrical conductivity is low, CF_3Br quickly vaporizes at atmospheric pressure and temperature, it is non-corrosive, and it is an effective suppressant at concentrations well below its toxicity level, rendering halon 1301 safe for humans and equipment in the event of a false discharge. Up until its production ceased in 1994, the cost of CF_3Br remained modest.

The highly desirable properties just mentioned led to CF_3Br being chosen for a multitude of fire protection applications. Now, faced with the elimination of this near-perfect agent, users and producers of fire suppression equipment are scrambling to identify suitable alternatives. The civilian and military aircraft industries have been particularly constrained in their choices because of severe weight and volume limitations and the disastrous consequences of a system which fails when called upon.

This article chronicles the research activities performed at NIST to identify agents to replace CF_3Br in certain aircraft applications (Grosshandler et al., 1994). The thermal, chemical and fluid mechanical properties of a dozen possible compounds were examined under static and dynamic conditions, and a protocol for selecting the most likely candidates for full-scale, live-fire testing was developed. Implications for future research into environmentally acceptable fire suppressants are discussed.

FIRE PROTECTION SYSTEMS

Two aircraft fire protection applications currently using CF_3Br have been investigated: engine nacelles and dry bays. Engine nacelles are the portions of an airframe which surround the main jet engines. They vary in shape and size but are typically annular

with a length and diameter of the same order as the engine they encase. Fuel and hydraulic lines, pumps and lubrication systems are located within the nacelle volume. Ventilation is provided to prevent the build-up of combustible vapors, and drain holes on the underside are used to reduce the amount of fluid that could pool following a leak. The engine's combustion chamber liner is isolated from the nacelle wall, but surface temperatures up to 700 °C can exist during operational extremes. Protection of the nacelle from an in-flight fire is currently provided by CF_3Br stored directly adjacent to the nacelle, or removed by tens of meters and piped to the fire zone, depending upon the availability of space. An example of a nacelle and fire suppression system is shown schematically in Figure 1.

The operational requirements for commercial and military engine nacelle protection are similar. Thermal sensors are used to determine when an abnormal, overheated condition exists in the nacelle region. In such a case, the flight of the airplane is leveled and the designated crew member arms the appropriate halon 1301 bottle and fires the release mechanism. The halon is stored under nitrogen at pressures in the range of 2 to 4 MPa. A system certification process requires that enough agent be available to maintain a minimum concentration (about 6% by volume) throughout the nacelle for a minimum time interval (about 0.5 s) to ensure that the fire will be extinguished and not relight. Many systems have a duplicate bottle to be used as a back-up should the first shot be unsuccessful.

Aircraft dry bays refer to normally closed spaces, often adjacent to flammable liquid storage areas and in which a combustible mixture and an ignition source could co-exist following penetration by an anti-aircraft projectile. The fire threat is unique to military aircraft. Dry bays vary considerably in volume, typically being in the range of 0.2 to 3.0 m³. They are located in the wings and fuselage, and their shape is most often irregular with aspect ratios up to 10:1 not uncommon. The bays may or may not be ventilated, and are usually cluttered with

Table 1. Thermodynamic properties of chemicals being evaluated (based upon references in Yang and Breuel, 1994)

Formula (Designation)	Boiling Point @ 101 kPa, °C	Vapor Press. @ 25 °C, MPa	Molec. Wt., kg/kmol	Δh_{fg} @ 101 kPa, kJ/kg	ρ_L (sat.) @ 25 °C, kg/m ³
C ₂ F ₆ (FC-116)	-78.2	- ¹	138	117	608 ¹
CF ₃ Br (halon 1301)	-57.8	1.61	149	111	1551
C ₂ HF ₃ (HFC-125)	-48.6	1.38	120	160	1190
CHF ₂ Cl (HCFC-22)	-40.9	1.05	87	229	1192
C ₃ F ₈ (FC-218)	-36.8	0.88	188	101	1321
C ₂ H ₂ F ₄ (HFC-134a)	-26.2	0.67	102	217	1209
CF ₃ I	-22.0	0.49	196	106	2106
C ₃ HF ₇ (HFC-227ea)	-16.4	0.47	170	131	1395
C ₂ HF ₄ Cl (HFC-124)	-13.2	0.38	137	162	1357
cyclo-C ₄ F ₈ (FC-318)	-7.0	0.31	200	112	1499
C ₄ F ₁₀ (FC-31-10)	-2.0	0.27	238	96	1497
C ₃ H ₂ F ₆ (HFC-236fa)	-1.5	0.27	152	150	1356

¹ Critical temperature is 19.7 °C; gas density computed at storage bottle conditions (25 °C and 4.1 MPa).

electronic, hydraulic and mechanical components. Compared to the events leading to engine nacelle fire suppression, the required timing is two orders-of-magnitude faster for dry bay protection. High-speed infrared detectors sense the initial penetration of the projectile and automatically arm and fire the halon bottle. The storage bottles are located directly in or adjacent to the protected space to minimize the time needed to flood the volume totally. The entire suppression sequence occurs in less than 100 ms and requires no crew intervention.

The design of the engine nacelle and dry bay fire protection systems is integrally dependent upon the unique characteristics of CF₃Br. To rationally select a replacement chemical for halon 1301 one must be able to predict the behavior of the material under all conditions to which it will be subjected. In addition to knowing how much of an agent is required to extinguish a flame, the following items must also be examined: the thermodynamic equation of state, pure and in mixtures with a pressurizing gas; flow regimes in pipes under transient conditions; formation of sprays and evaporation in air; entrainment into the combustion zone; conditions leading to combustion enhancement; suppression by-products; compatibility of the agent with aircraft materials; and long term stability. Other parameters that greatly affect the selection process are unrelated to actual performance in the aircraft. These include the agent's ODP, atmospheric lifetime, acute and chronic toxicity, manufacturability, and cost.

PERFORMANCE OF ALTERNATIVE AGENTS

A number of studies have been conducted to identify potential replacements for halons. Pitts et al. (1990) reviewed the developmental process that originally led to the selection of CF₃Br (e.g., Purdue Research Foundation, 1950) and suggested over 100

compounds that might act as a satisfactory alternative in the future. The following classes of compounds were included: saturated and unsaturated halocarbons; halogenated hydrocarbons containing single- and double-bonded oxygen; sulfur halides; phosphorous compounds; silicon and germanium compounds; metallic compounds; and inert gases. Zallen (1992) produced a narrowed list for the specific applications of interest to the Air Force. As a class, the halocarbon family provides a number of low ODP chemicals with physical properties closely akin to CF₃Br that could be engineered into existing fire protection systems as early as 1996.

Eleven chemicals were selected to examine in detail, including fluorocarbons (FCs), hydrofluorocarbons (HFCs), hydrochlorofluorocarbons (HCFCs), and an iodofluorocarbon (IFC). The molecular weight, liquid density, normal boiling point, vapor pressure at 25 °C, and enthalpy of vaporization at 101 kPa for the agents are listed in Table 1. Additional thermodynamic properties can be found in the reference by Yang and Breuel (1994).

Fire Suppression Effectiveness

The conventional method to determine the minimum amount of agent necessary for suppression of a liquid fuel fire is to slowly increase the concentration in a low velocity air stream flowing concentrically over a small (≈ 25 mm diameter) burning pool. This apparatus, referred to as a cup burner, has been used for evaluating halon 1301 and other flame extinguishants (e.g., Booth et al., 1973). The fires of interest for the specific application of aircraft protection are unsteady and turbulent, and are characterized by a wide range of possible initial and boundary conditions. Hamins et al. (1994) looked at suppression mechanisms and

described different facilities used to cover various fuels and flame geometries. The cup burner cannot simulate the combined droplet evaporation and turbulent mixing which might occur in a realistic engine nacelle or dry bay fire.

A turbulent spray burner, described by Grosshandler et al. (1995), was designed to produce a complicated flame structure in which fuel droplets vaporize and react with an oxidizer that can be composed of either pure air, or air mixed with combustion products and/or fuel vapor. The mass fraction, total mass, and minimum volume of agent required to extinguish a given flame must all be considered when ranking the effectiveness of different fire fighting agents. Of the alternatives to halon 1301 evaluated in the turbulent spray burner, CF_3I required the least mass to extinguish the flame, followed by N_2 . The next most efficient halocarbon was CHClF_2 ; C_4F_{10} required the most mass, over twice that of CF_3Br . The spread between the least and most effective (non-iodine-containing) fluorinated alternatives (on a mass basis) was not large, but was greater than the uncertainty of the results ($\pm 10\%$). On a volume basis, the IFC and two HCFCs were the best, and nitrogen was the poorest performer.

The alternative agents performed better in the turbulent spray burner relative to halon 1301 than was predicted from cup burner measurements. It is suspected that this is due to the higher strain rates present in the spray burner and the reduced amount of time for the bromine atom in halon 1301 to chemically inhibit the combustion process. The total mass of suppressant required for flame extinction was found to decrease to a limiting value, in all cases, as the injection interval decreased.

A shock wave preceding a turbulent flame can occur in a combustible mixture that is confined in a space when the composition falls within an appropriate range. Obstructions in the flow can promote intense mixing of the fresh reactants with the combustion products and can cause pressure waves to interact with the mixing region. Given enough distance, the flame may accelerate dramatically, reaching a supersonic regime of flow and producing a quasi-detonation. Certain geometries of aircraft dry bays might lead to such a sequence of events. The effectiveness of a fire fighting agent in suppressing a quasi-detonation can be rated by the extent to which it decelerates the propagating wave and simultaneously attenuates the shock pressure ratio.

Because the fire extinguishant is unlikely to be released prior to the establishment of a turbulent flame, the traditional experiment in which the flame inhibitor is premixed with the fuel and air prior to ignition does not replicate the chemistry critical to the actual situation. Each dry bay on an aircraft has a different geometry, and the release of the agent once a fire is detected is highly variable. The complexities and biases associated with the fluid dynamics of release can be avoided by premixing the agent with the fuel and air in a portion of the tube distinct from where the flame is initiated.

A two-section, deflagration/detonation tube was designed to produce the desired environment for both the flame initiation and combustion suppression regimes. A repeatable, uninhibited turbulent flame was fully established in the driver section, which was filled with the combustible mixture only. The ignition energy was provided by a spark. Spiral-shaped obstructions produced an area blockage ratio of 44%, which promotes a quasi-detonation

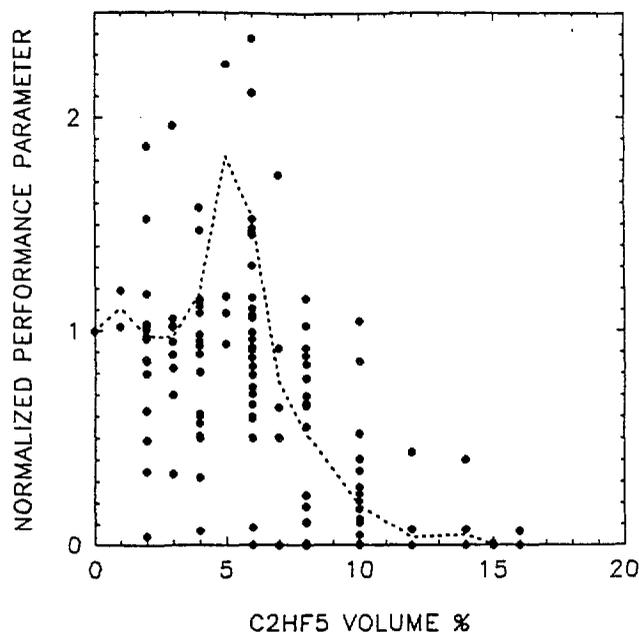


Figure 2. Effectiveness of C_2HF_5 in suppressing combustion within detonation, tube as a function of volume fraction.

prior to entering the test section. The suppressant was premixed with the same fuel-to-air ratio in the 50 mm diameter, 5 m long test section. Piezoelectric transducers measured the shock pressure ratio and Mach number, and photodiodes recorded the presence of radiation. Details of the facility and experimental design have been presented elsewhere (Hamins et al., 1994; Gmurczyk and Grosshandler, 1995).

Hundreds of experiments were run using ethene and propane under rich, stoichiometric and lean conditions, and using different halocarbons for the suppressant. Figure 2 summarizes the performance of C_2HF_5 as a function of the volume fraction of agent in the test section. The performance parameter plotted on the ordinate is the ratio of the shock speed, radiation wave speed, and shock pressure measured with agent present, normalized by the value of the respective parameter when no inhibitor is present. The dotted line in the figure represents the average of multiple measurements at the same agent concentration. A value of zero on the abscissa corresponds to the uninhibited condition. No change was found when the volume fraction was increased above 20%.

It was found generally that the presence of hydrogen in a molecule increased the pressure ratio over a large concentration regime. That is, unless a sufficient amount of the chemical is added to the mixture, the presence of agent can exacerbate the situation. The peak at 5% concentration of C_2HF_5 seen in Fig. 2 is indicative of this effect.

Iodine appears to be released by the passage of the shock wave, and inhibits the flame effectively. Non-monotonic response of the performance parameter to increasing the concentration of CF_3I was found, suggesting that there are competing reactions, with the I-atom either inhibiting or accelerating the combustion depending upon the concentration of the agent. The relatively

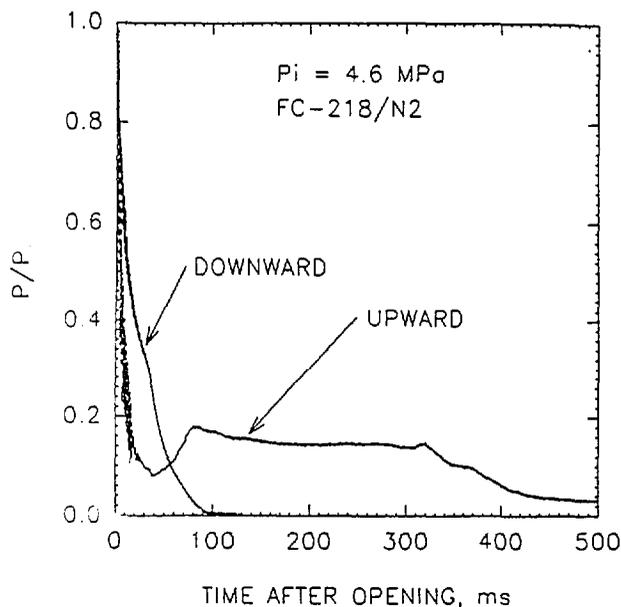


Figure 3. Pressure history of C_3F_8/N_2 discharging from 0.5 liter bottle, comparing upward to downward orientation.

poorer showing of CF_3I in the detonation tube experiments, when compared with suppression studies in constant pressure flames, highlights the different chemical kinetic pathways which dominate each system.

Thermodynamic Properties

Knowledge of the mechanical equation of state is essential to design a storage system for an alternative fire suppressant. A high liquid density at room temperature is desirable because it permits a smaller size vessel to be used for the required mass of agent. On board an airplane, the storage vessel may be subjected to temperature swings between $-60\text{ }^\circ\text{C}$ and $150\text{ }^\circ\text{C}$. If the saturation pressure is too low at cold temperatures, the agent will not be propelled from the container at a rate fast enough to be effective on the fire (although this can be compensated by increasing the amount of N_2). If the vapor pressure is too high at elevated

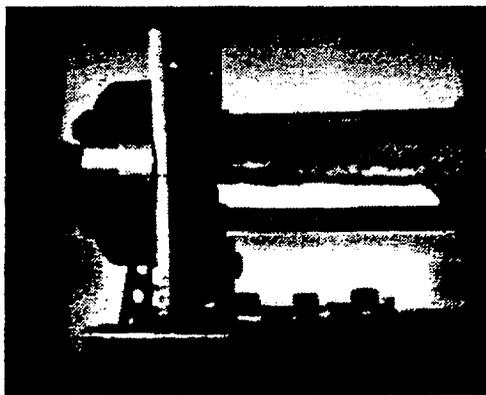


Figure 4. Photograph of C_3F_8/N_2 discharging horizontally from 0.5 liter pressure vessel 100 ms after opening.

temperatures, the storage container can burst.

P-v-T data were gathered (Yang and Breuel, 1994) in a fixed 50 ml volume stainless steel vessel for each of the chemicals evaluated. With the container 1/3 filled with liquid agent at room pressure, the maximum pressure experienced at $150\text{ }^\circ\text{C}$ was just under 11 MPa. This exceeds the minimum proof pressure currently specified (MIL-C-22284A) for fire extinguisher bottles filled with CF_3Br , pointing to the safety hazard posed by insufficient knowledge of an accurate equation of state.

The pressure in the vessel at low temperatures dropped well below atmospheric for all the chemicals examined but one. Normally, nitrogen is added to existing halon bottles to ensure rapid discharge even when the temperature is low. Additional P-v-T measurements were taken with differing amounts of N_2 mixed with the twelve suppressants to determine the solubility. The Peng-Robinson equation of state was used to fit the data.

A computer program called PROFISSY (Yang et al., 1995; Gann et al., 1995) was developed as a design aid for fire protection equipment manufacturers. It is based upon the comprehensive thermodynamic data base established at NIST for refrigerant mixtures, which is available as the computer code REFPROP (Gallagher et al., 1993).

Sudden Discharge Process

The quick release and delivery of the suppressant is particularly critical for dry bay protection, where events leading to a threatening over-pressure occur in less than 50 ms. The behavior of the agent during conditions of vessel blow-down and the characterization of the dispersion, mixing and evaporation of the resulting two-phase turbulent jet have been investigated by Pitts et al. (1994). Cylindrical and spherical pressure vessels with internal volumes of about 1/2 liter were equipped with fast-acting solenoid valves and rupture discs with opening diameters in excess of 12 mm. One vessel was made of acrylic and another equipped with a glass window to permit visual inspection of the material inside the bottle during the actual discharge process.

In downward discharges, mass emptied from the bottles at rates over 10 kg/s; pressures dropped to 50 % of their initial value (typically 4 MPa) within 15 ms. Except for C_2F_6 (which has a critical temperature below ambient), the liquid volume flow rate was found to be almost independent of the agent type. The solid curve in Figure 3 is a trace of the pressure measured during the discharge of the 0.5 liter acrylic vessel, filled half way with liquid C_3F_8 , and pressurized initially with N_2 to 4.6 MPa. The change in curvature at 35 ms corresponds to the point where the liquid has been exhausted. Nitrogen gas mixed with agent vapor flows for another 65 ms.

The volume flow rate of liquid was found to increase directly with the area of the opening, and directly with the square root of the initial pressure, which would be the behavior expected for a pure, single-phase liquid. This implies that boiling did not occur during the initial period of blow-down.

Rotating the bottle so that the discharge was horizontal or upward greatly affected the pressure history and mass flow rate of agent. Figure 4 is a photograph of a horizontal discharge of C_3F_8 , initially pressurized with N_2 to about 4.5 MPa, taken 100 ms after the 19 mm diameter exit disc has ruptured. The initial pressure

drop was faster than for the downward discharge because the nitrogen vapor had direct access to the exit opening. About 20 ms into the event the ullage changed from clear (gas only) to foggy, indicating that condensation occurred as the temperature dropped due to isentropic expansion.

Following the rapid blow-down, the mass flux of agent was limited by the rate at which heat could be supplied to maintain pool boiling. For a low boiling point compound like C_3F_8 the pressure recovers (see dotted curve in Fig. 3) after the nitrogen has been exhausted because the rate of boiling is relatively high. The mass flow of higher boiling point compounds was substantially lower, and the time for total discharge in the upward direction was greater than downward discharge by almost an order of magnitude.

The nitrogen pressurizing gas was only partially dissolved in the tests described above. More recent experiments with downward discharges have been conducted with the N_2 and agent equilibrated. For 5 ms after the disc ruptured, a clean interface delineated the compressed liquid agent from the nitrogen vapor. Shortly thereafter (the exact time interval increased with the boiling point of the agent), the entire volume became foggy, suggesting that the nitrogen was being released due to the drop in pressure, producing a froth which filled the inside of the vessel. It was not possible to compare the mass loss rate for the N_2 -equilibrated and the unequilibrated experiments.

The behavior of the agents external to the vessel was also examined during the sudden discharge process (Pitts et al., 1994). If N_2 was only partially dissolved in the agent, higher boiling point compounds such as C_4F_{10} flowed for about 10 ms like water in a stream, with a diameter about equal to the exit, followed by a narrow spray which lasted at least another 20 ms. Low boiling point compounds like CF_3Br established a conical spray almost immediately, with a half angle greater than 30° .

The appearance of the spray could be grouped by the Jakob numbers of the individual agents, where Ja is the ratio of the change in enthalpy between the ambient temperature and normal boiling point, to the enthalpy of vaporization at atmospheric pressure. Halon 1301 at $20^\circ C$ has a Ja of 0.51, which implies that 49% of the heat required to vaporize the agent must be extracted from the surroundings. The values of Ja for the other agents range from 0.59 for C_3F_8 (more easily vaporized) to 0.16 for $C_3H_2F_6$ (more difficult to vaporize).

The arrival of the head of the spray at different axial locations was monitored by the attenuation of laser light. By dividing the distance between two adjacent laser beams by the time of arrival of the attenuating spray, the velocity of the jet could be estimated. Figure 5 is an example of the type of data gathered using C_3F_8 . The open circles represent the decrease in velocity of the spray head as a function of distance downstream of the storage vessel for an ambient temperature discharge. The velocity drops from a maximum of 65 m/s, 20 cm downstream of the 19 mm diameter exit, to 35 m/s, 120 cm downstream. The solid symbols are the velocity measured in an identical test, but with the storage vessel cooled to $-45^\circ C$. The pressure in the storage bottle was held constant for the two tests during the filling process, which led to a substantially reduced value when the bottle was cooled. The spray velocity is much lower near the exit of the vessel when the agent is cooled because less material has vaporized. By a location

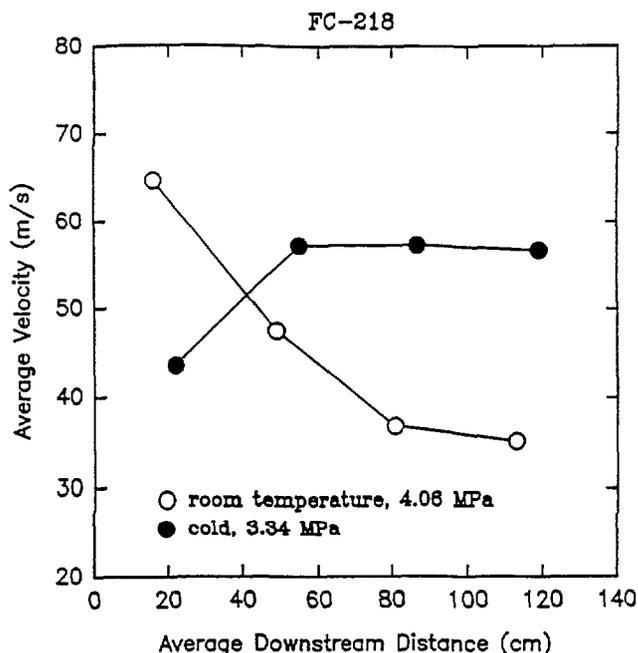


Figure 5. Velocities at head of developing spray during sudden discharge of C_3F_8/N_2 , comparing 22 to $-45^\circ C$ bottle temp.

60 cm downstream, however, the colder spray is travelling significantly faster, and remains faster to the end of the measuring volume. This reversal is attributed to delayed evaporation. If one desires to fill a space fully and quickly with a vaporized fire fighting substance, the room temperature behavior is more desirable. However, if one wishes to throw the agent a long distance more quickly, the behavior exhibited by the cold agent would be preferred.

Flow Through Piping

The fire suppression bottles used to protect engine nacelles are located a half to ten meters away (see Fig. 1). A solenoid valve or explosive squib releases the contents of the bottle into a distribution manifold. The success of the system depends upon the rate of delivery and the distribution of the agent within the nacelle volume. All new systems must be certified (by the FAA or DoD) that a concentration sufficient to extinguish a fire anywhere in the nacelle can be maintained for 0.5 seconds. Normally, only systems containing CF_3Br can be certified; however, C_2HF_5 will be used as a surrogate by the Navy in the future to avoid non-essential discharges of CF_3Br (Leach and Homan, 1995).

Cleary (Gann et al., 1995; Cleary et al., 1995) describes an experimental facility (see Fig. 6) for evaluating the discharge of alternative suppressants in various piping systems. The agent is stored in a 4 liter cylindrical pressure vessel capable of operating up to 14 MPa. A quick-opening solenoid valve located at the bottom of the vessel turns the flow 90° through a minimum open diameter of 32 mm. A smooth transition section reduces the diameter to 16 mm and connects to a test section which can be varied up to 4 m in length, and which contains a transparent section to view the flow. Pressure transducers are located along

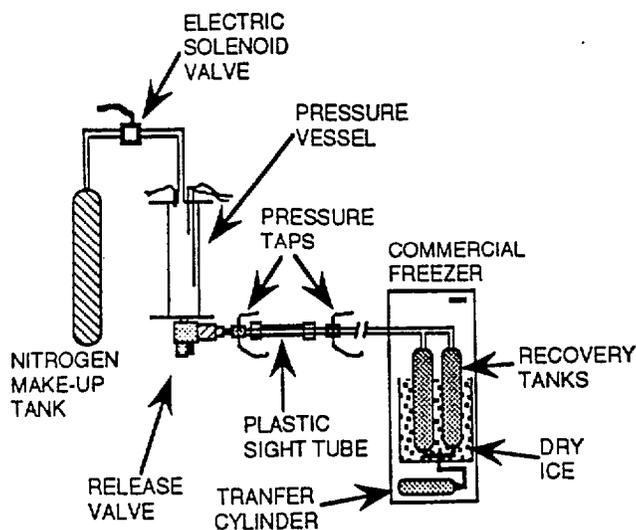


Figure 6. Schematic of pipe flow discharge system.

the test section. The outlet of the test section empties into a 15 liter recovery tank maintained at dry ice temperature. Recondensed agent is collected at the bottom of the recovery tank for recycling. High pressure nitrogen may be supplied to the agent storage vessel to maintain a constant head during discharge.

Figure 7 is an example of the data taken during a constant head discharge test. The test section and recovery tank are initially at 0.1 MPa and the storage vessel is filled with CF_3Br to 2.5 MPa. The outlet valve is opened 1000 ms into the test, followed immediately by the opening of the inlet N_2 make-up gas

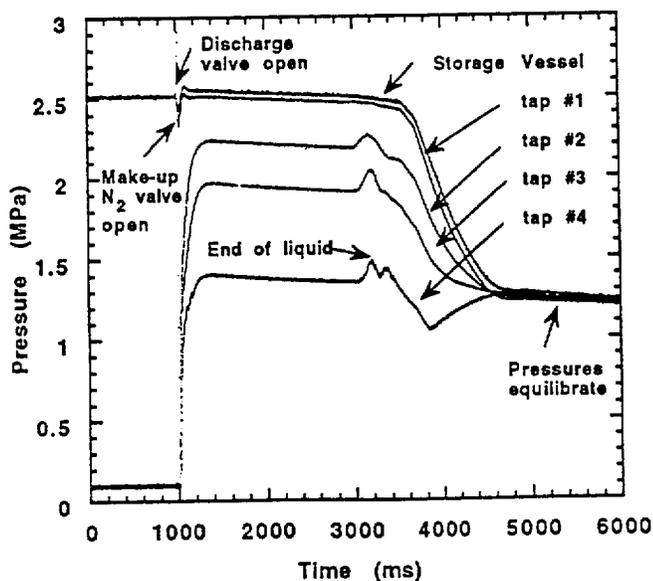


Figure 7. Pressure as a function of downstream position during constant-head discharge of CF_3Br into 9.5 mm dia., 3 m long tube.

valve. The pressure in the storage vessel is maintained constant for over two seconds while the piping test section fills with liquid agent. Pressure tap #1 is just downstream of the release valve; pressure taps #2 through #4 are located, progressively, one meter further downstream in the 9.5 mm diameter pipe. The increase in pressure first noticeable 3000 ms into the test at tap #2 is a result of the liquid having been emptied from the line and the nitrogen gas being liberated. The inlet nitrogen valve is closed at 3500 ms, at which point the gas flow diminishes and the pressure adjusts to a single equilibrium value.

Fixed mass discharges were run to simulate an actual fire suppression piping system. The effect of pipe geometry (9.5 and 16 mm diameter, length up to 4 m, bends, expansions, contractions and tees), agent type (CF_3Br , C_2HF_5 , C_3HF_7 , and CF_3I), and initial conditions (pressures from 2.2 to 5.9 MPa, liquid volume in vessel from 48 to 70%) on the pressure drop and time to liquid-empty conditions were investigated. A quasi-steady, equilibrium model was developed by Cleary (Gann et al., 1995; Cleary et al., 1995) to predict the transient discharge process. Sample calculations have been made to demonstrate the model's ability to assist in the selection of the size of the storage vessel and distribution piping to meet current certification requirements.

Other Performance Factors

The chemicals investigated in this study produce hydrofluoric acid when added to a flame, although the amount formed from CF_3I is significantly less than from the others. Incompatibilities were identified in some agent/metal and agent/polymer combinations, but for all eleven alternatives there are materials that could be used for the piping and vessel design, and the impact of a false discharge on the aircraft structure would be minimal. The stability during storage for at least a year appears not to be a serious limitation to any of the chemicals.

All the alternatives have ODPs well below the maximum permitted by the EPA. Long atmospheric lifetimes (greater than 1000 years) are a concern for the perfluorocarbons. Adverse toxicological effects at concentrations less than the amount required for suppression were found to be present in a number of the non-perfluorocarbons, but none severe enough to preclude use of the chemical in a unoccupied space such as an engine nacelle.

The agents considered are currently in production to at least the pilot scale, and most likely could be provided in quantities if selected as an alternative to CF_3Br . The current price of the different agents varies significantly, but should not be a major factor in the decision process since the price structure would be greatly altered following the selection of a particular compound.

RECOMMENDED AGENTS

Of the alternatives examined, only CF_3I suppressed the atmospheric pressure laboratory flames as well as CF_3Br . The other agents required liquid storage volumes two to four times as great, with C_2HClF_4 being the most effective in the flames and C_4F_8 and C_2F_6 among the least effective.

The Jakob number was chosen as a good indicator of the ability of the agent to vaporize quickly and disperse throughout the protected volume. Dispersion, especially at reduced temperatures, was felt to be a significant discriminator among the alternatives.

The compounds with the highest Ja are C_3F_8 and C_2HF_5 ; $C_3H_2F_6$, C_2HClF_4 , and CF_3I have the lowest values of Ja.

The chemicals recommended in the NIST study (Grosshandler et al., 1994) for full scale testing by the Air Force were C_3F_8 , C_3HF_7 , C_2HF_5 , C_2HF_4Cl , and CF_3I . The chlorine-containing chemical was eliminated from the full-scale test program because it had the highest ODP and a low value for Ja. Following a year of live-fire tests in the Wright-Patterson AFB full-scale facility, C_2HF_5 was recently chosen for the final design study.

FUTURE RESEARCH EFFORTS

Why continue the search for alternative suppressants? There are at least four answers to this question: (1) inefficiency - the above gaseous agents require over twice as much storage volume as halon 1301, depending upon the specific application; (2) flexibility - different fire threats require different, and possibly customized, suppression strategies; (3) collateral damage - HF is created during suppression with the selected gaseous agents in concentrations an order of magnitude larger than found during suppression with CF_3Br ; and (4) changing environmental regulations - the EPA and international environmental organizations are concerned about long atmospheric lifetimes, suggesting further regulations are likely.

Many industries and government operations have suffered from the phase out of halons, but none as severely as the Department of Defense. The DoD has committed itself to protecting their ground and mobile facilities against fires and explosions in a manner which complies with all future environmental regulations. A multi-year research plan is being formulated (Gann, 1995) which is aimed at developing long-term options to minimize the impact of fire protection on their mission. The research will be comprised of multiple technical thrusts, including risk assessment and selection criteria, fire suppression principles, new concepts and emerging technology advancement, suppression optimization, and testing at the laboratory scale with real-scale validation. This plan is designed to establish a broad understanding of the suppression process and a diversity of tested approaches. While driven by the specific needs of the military, the scientific understanding and many of the technologies developed should be directly applicable to civilian needs and should benefit the entire fire protection industry.

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REFERENCES

Booth, K., Melia, B.J., and Hirst, R., 1973, *Critical Concentration Measurements for Flame Extinguishment Using a Laboratory "Cup Burner" Apparatus*, ICI Mond Division, Wilmington Laboratory, August 31.

Cleary, T., Yang, J., King, M., Boyer, C., and Grosshandler, W., 1995, "Pipe Flow Characteristics of Alternative

Agents for Engine Nacelle Fire Protection," *Halon Options Technical Working Conference*, University of New Mexico, Albuquerque, May.

Gallagher, J., McLinden, M., Huber, M., and Ely, J., 1993, *NIST Standard Reference Database 23: Thermodynamic Properties of Refrigerants and Refrigerant Mixtures Database (REFPROP)*, Version 4.0, U.S. Dept. of Commerce, Washington.

Gann, R., 1995, "Next-Generation Fire Suppression System Technology: A National Research Plan," *Halon Options Technical Working Conference*, University of New Mexico, May.

Gann, R., et al., 1995, *Fire Suppression System Performance of Alternative Agents in Aircraft Engine Nacelle and Dry Bay Laboratory Simulations*, NIST Special Publication, in press.

Gmurczyk, G., and Grosshandler, W., 1995, *Twenty-fifth Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, pp. 1497-1503.

Grosshandler, W., Gann, R., and Pitts, W., eds., 1994, *Evaluation of Alternative In-flight Fire Suppressants for Full-scale Simulated Aircraft Engine Nacelles and Dry Bays*, NIST SP 861, Nat. Institute of Standards and Technology, Gaithersburg, April.

Grosshandler, W., Presser, C., Lowe, D., and Rinkinen, W., 1995, *Journal of Heat Transfer* 117, pp. 527-532.

Hamins, A., Gmurczyk, G., Grosshandler, W., Rehwoldt, R., Vazquez, I., Cleary, T., Presser, C., and Seshadri, K., 1994, "Flame Suppression Effectiveness," Section 4, NIST SP 861.

Harrington, J.L., 1993, *NFPA Journal*, pp. 38-42, March/April.

Leach, W., and Homan, J., "U.S. Navy Halon Simulant Identification Program," *Halon Options Technical Working Conference*, University of New Mexico, Albuquerque, May.

Pitts, W., Nyden, M., Gann, R., Mallard, W., and Tsang, W., 1990, *Construction of an Exploratory List of Chemicals to Initiate the Search for Halon Alternatives*, NIST TN 1279, Nat. Institute of Standards and Technology, Gaithersburg, August.

Pitts, W., Yang, J., Gmurczyk, G., Cooper, L., Grosshandler, W., Cleveland, W., and Presser, C., 1994, "Fluid Dynamics of Agent Discharge," Section 3, NIST SP 861.

Purdue Research Foundation and Department of Chemistry, 1950, *Final Report on Fire Extinguishing Agents*, AD 654322, Purdue University, West Lafayette, July.

Westbrook, C.K., 1982, *Nineteenth Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, pp. 127-141.

World Meteorological Organization, 1989, *Scientific Assessment of Stratospheric Ozone: 1989*, Report No. 20, Alternative Fluorocarbon Environmental Acceptability Study.

Yang, J., Boyer, C., and Huber, M., 1995, "PROFISSY - A Computer Code for Calculating Alternative Agent/Nitrogen Thermodynamic Properties," *Halon Options Technical Working Conference*, University of New Mexico, Albuquerque, May.

Yang, J., and Breuel, B., 1994, "Thermodynamic Properties of Alternative Agents," Section 2, NIST SP 861.

Zallen, D.M., 1992, *Halon Replacement Study*, SBIR Report ZIA-92-001, Aeronautical Systems Division, Wright-Patterson AFB, Zallen International Associates, Albuquerque, February 28.