INTRODUCTION

Initiated in 1997, the Department of Defense’s Next Generation Fire Suppression Technology Program (NGP) has completed its seventh year of research. The NGP goal is to

“Develop and demonstrate technology for economically feasible, environmentally acceptable and user-safe processes, techniques, and fluids that meet the operational requirements currently satisfied by halon 1301 systems in aircraft.”

Fires and explosions continue to be among the greatest threats to the safety of personnel and the survivability of military aircraft, ships, and land vehicles in peacetime and during combat operations. However, over the past six years, research to identify replacement fire suppressants has declined considerably, within the NGP, domestically and internationally, despite the continuing need. To date no commercial or military aircraft have had their halon 1301 systems replaced, while new systems are being installed in the cargo bays of commercial jetliners. Meanwhile, the international community is continuing to cast an eye on the necessity of maintaining the large halon 1301 reserves and even considering the requirement of a total phaseout. Thus, the demands on research to identify new approaches to aircraft fire suppression are unabated, nor have the demands on the new technologies lessened.

NGP technology is already having an impact on aircraft fire suppression systems, and NGP research has generated unparalleled contributions to the published literature, all of which can be obtained via the NGP web site: www.bfrl.nist.gov/866/NGP. Much of the most recent progress is being reported at this Conference.

TECHNICAL PROGRESS

New Flame Suppression Chemistry

The NGP continues to examine systematically the most promising chemical families. While this search has produced additional knowledge of what makes a good suppressant, to date we have not identified a likely successor to halon 1301 for in-flight aircraft fires. The list of criteria to guide the search is:

1. Fire suppression efficiency at least comparable to halon 1301 (about 3 % by volume) and certainly higher than the hydrofluorocarbons (HFCs). Based on prior experience, this focuses the search on compounds that contain at least one bromine, iodine or phosphorus atom, although other possible functionalities can arise.
2. Short atmospheric lifetime (current preference of the order of a month), to keep ozone depletion potential (ODP), global warming potential (GWP) and any future unidentified environmental contamination issues to a minimum.

3. Boiling point sufficiently low that for gaseous agents, an extinguishing concentration can be achieved within a specified time following discharge. An approximate theoretical upper limit is near 30 °C if the minimum temperature in flight is -40 °C.

4. Low toxicity relative to the concentration needed for suppression.

With regard to criterion 3, an effort is underway to improve understanding of the actual aircraft temperatures at which halon 1301 has been deployed. Data from incidents of halon release from all three services have been gathered. They document the altitude at which each release occurred, and we are converting this to an approximate temperature. The results will help refine the selection criterion for agent volatility, provide guidance to the dispersion optimization project, and assist platform managers in their selection of suppressant for their particular aircraft.

A rapidly released suppressant fluid disperses partially as droplets and partially as a gas. The high momentum droplets can fill a volume rapidly. For halon 1301, the droplets flash vaporize, completing the efficient dispersion of a gaseous suppressant. Thus all of the suppressant contributes to the effective concentration at the fire zone. For a chemical with a higher boiling point and/or a higher heat of vaporization, more of the fluid reaching the fire may still be in the liquid phase. Larger droplets may impact and stick to cold surfaces, may not flash vaporize en route to the flames, and also may pass through the flames without vaporizing fully. Thus, some (or even much) of the agent may not contribute to the effective concentration in the fire zone. To compensate for this, the mass of the fire suppression system may need to be increased significantly, either by carrying a larger mass of agent or by heating the storage and delivery hardware. Thus, given knowledge of the (low) ambient temperature, it is important to be able to estimate the true effective concentration of a potential halon alternative. This involves droplet evaporation time, flame zone residence time, and saturation vapor pressure. Using the Fire Dynamics Simulator, we are simulating the degree of vaporization of various aerosols in a simulated engine nacelle and developing criteria for the physical properties that lead to an acceptable suppression efficiency. The input conditions for the engine nacelle reflect an expected range of agent deployment conditions: incoming air temperatures from 298 K to 233 K, nacelle interior temperatures from 298 K to 373 K, input air flow velocity of 1 m/s, mean suppressant drop size of ca. 20 µm, and vapor fraction immediately following release of the pressurized agent between 0.2 and 0.7. The results will lead to the ability to estimate the true effective concentration of suppressant in a two-phase dispersion.

Sensitization to cardiac arrhythmia is recognized as the primary toxic effect of the halogenated compounds that dominate the search for halon alternatives. Estimating the cardiac sensitization concentration for a single compound or for a series of related compounds can have a major impact on whether an effective and safe alternative suppressant is identified. If a chemical is preferentially soluble in a barely polar liquid such as octanol, and less soluble in a polar fluid such as water, it may be more likely to accumulate in heart nerve and muscle cells membranes and cause cardiac arrhythmia. Determination of the octanol-water partition coefficient, K_{OW}, is rapid and requires only a few mg of the compound. Examining the data for volatile anesthetic
gases (Table 1) shows some potential for a possible correlation between $K_{OW}$ values and the occurrence of cardiac arrhythmia.

Table 1. Anesthesia Compounds – Partitioning and Arrhythmia Properties\textsuperscript{1,2}

<table>
<thead>
<tr>
<th>Property</th>
<th>Halothane</th>
<th>Enflurane</th>
<th>Isoflurane</th>
<th>Desflurane</th>
<th>Sevoflurane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil-water Ratio\textsuperscript{a}</td>
<td>220</td>
<td>120</td>
<td>170</td>
<td>19</td>
<td>55</td>
</tr>
<tr>
<td>Arrhythmia\textsuperscript{b}</td>
<td>+++</td>
<td>+</td>
<td>+</td>
<td>~</td>
<td>~</td>
</tr>
</tbody>
</table>

\textsuperscript{a} The "oil" phase is commonly, but not exclusively, octanol.
\textsuperscript{b} The symbols "+++," "+," and "~" reflect, in order, a decreasing tendency of the anesthetic to induce premature ventricular contractions in human patients during anesthesia. The last of these indicates only a slight tendency.

The current phase of the examination of chemical families for potential CF$_3$Br replacements is following the general guidance from the most recent assessment of the field.\textsuperscript{3}

- Last year, the NGP examined seven phosphorus-containing compounds (PCCs). Four of these appeared to be stable. However, despite substantial fluorination, the lowest boiling point ($T_b$) was 42 °C, and further examination of the PCCs awaits resolution of the boiling point criterion.
- To determine whether there is reason to pursue the metal-containing compounds further, the NGP is investigating the features that lead to effective chemical action in quenching flame chemistry and the features that can limit the concentration of the active species in the flame zone.
- Recognizing the importance of the binding energy of a suppressant to one of the free radicals that participate in the chain branching chemistry of flame propagation, we have conducted computation studies to elucidate the specific desirable values. The cases studies were the binding of bromine and hydrogen atoms, sodium with hydroxyl radicals and iron with oxygen atoms, all examined in a stoichiometric methane-air mixture. The binding energies were varied about the accepted values, and the resulting effect on the flame velocity was assessed. It was concluded that the bond energy between a catalytic scavenger and a flame radical must be in the range of 300 kJ/mole to 400 kJ/mole.

The most promising remaining new chemicals are generally bromine containing for efficient flame quenching and fluorinated to keep boiling points low. The nitrile group (-CN) has been described as a "pseudohalogen," so compounds containing this functionality are being explored as well. In particular, members of the following families are in the process of being acquired for flame extinguishment testing:

- Fluoronitiriles and bromofluoronitiriles. CF$_3$CN has a $T_b$ of -64 °C. The flame extinguishment performance for this chemical and the full family is unknown, so this

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\textsuperscript{2} \url{www.virtual-anaesthesia-textbook.com/vat/volatile.htm}.
result could open an unanticipated direction for a new candidate. CF$_2$BrCN is expected to have a suppression efficiency at least comparable to halon 1301; its $T_b$ is only 3 °C. The atmospheric lifetimes of the nitriles are expected to be short due to hydrolysis of the CN group.

- **Bromofluoropropene oxides (oxiranes).** These compounds are expected to have short atmospheric lifetimes, but this needs to be confirmed. The lowest boiling points are estimated to be between 0 °C and 10 °C.

- **Bromofluoropropenes.** The atmospheric lifetimes should be low since the double bond is reactive in the troposphere. The calculated log $K_{OW}$ values are near that of halon 1301 for all possible penta-, tetra- and trifluorinated bromofluoropropenes. We are also seeking to obtain the three fully halogenated compounds with the lowest calculated $K_{OW}$ values: CFBr=CFCF$_3$ ($T_b = 27$ °C), CF$_2$=CBrCF$_3$ ($T_b = 25$ °C), and CF$_2$=CFCF$_2$Br.

- **Bromofluoroethers.** They are expected to have relatively low toxicity and good flame extinguishment properties but will require some degree of hydrogenation to minimize ODP impact. Prime candidates are CBrF$_2$-O-CF$_3$, ($T_b$ ca. -30 °C to -8 °C), CBrHF-O-CF$_3$ and CBrF$_2$-O-CHF$_2$ (predicted to boil in the range 5 °C to 15 °C) and CBrF$_2$-O-CF$_3$.

**Improved Suppressant Delivery**

Prior NGP research had developed new types of solid propellant fire extinguishers (SPFE) that have both reduced combustion temperatures and increased flame suppression efficiency, which in turn will enable freedom of selection of the momentum of the suppressant stream. These have now been examined further. The combination of propellants based on the advanced high nitrogen propellant BTATZ ($C_4H_4N_{14}$) and incorporation of coolant species into the propellant composition reduces exhaust temperatures by as much as 30 % vs. current baselines. The incorporation of potassium carbonate in the solid propellant composition decreases by up to a factor of three the mass of suppressant needed to extinguish mid-scale flames. Fire testing using hybrid fire extinguisher (HFE) configurations, in which the coolant or chemical additive is added downstream of the combusting propellant, showed that high-boiling agents can be delivered even at low temperatures, their low vapor pressures offset by the heating and pressurizing power of the solid propellant driven HFE. This has produced an additional ca. 30 % increase in mass efficiency (Figure 1). Hydrofluorocarbons and hydrofluoroethers were comparably effective on a mass basis.

Tests in several military platforms were used to evaluate the effectiveness of SPFE technology. These test series typically included side-by-side testing of both inert and chemically active SPFE systems. While these test series differed in bay size, clutter, airflow, fuel flow rate and pre-burn conditions (and therefore fire threat), the resulting threshold successful propellant masses show a consistent benefit.

These results show the validity both of the mid-scale test facility used to screen SFPE formulations and, more importantly, of the large improvements in efficiency from the NGP-developed SFPE technologies. The improved mass efficiency enables:

- Greater flexibility in design, which can translate into a reduced number of different
SPFE configurations on a given aircraft, resulting in lower per unit costs and also lower logistics costs;

- Simplified existing fire protection system configuration by using a lesser number of different sizes of SPFEs; and
- Opportunities to upgrade fire protection system performance without substantive changes to the platform.

Figure 1. Side-by-Side Testing of Inert and Chemically Active (CA) SPFEs on Sub-scale (FTF) and Full-Scale Military Aircraft Platforms [blue bars: inert effluent, yellow bars: 1st generation chemically active systems; green bars: 2nd generation chemically active systems]

NGP experiments with CF$_3$I ($T_b = -22$ °C) discharges into a simulated engine nacelle at -40 °C have shown that inefficient dispersion should be expected when discharging a suppressant fluid into a system whose temperature is well below the fluid boiling point. Much of the liquid deposited on the nacelle floor and evaporated over many seconds. Thus, basing the design mass of agent for an engine nacelle on room temperature test data could lead to significant underestimation of the mass needed for in-flight fire suppression. Current work is directed at generalizing these results to a broader range of fluid boiling points and to different temperature differentials. The next combination will be CF$_2$Br$_2$ ($T_b = 24.6$ °C) discharged into the NIST nacelle simulator at room temperature and 0 °C. This compound was selected for its physical properties and ease of detection.

We have completed a series of experiments to provide data regarding the behavior of suppressant droplets as they encounter a single well-defined cylindrical obstruction in their path. These results become the basis for interpreting the interactions with complex clutter and for the
treatment of aerosol suppressants in suppressant flow modeling. Experiments were performed with water ($T_b = 100 \, ^\circ$C), HFE-7000 ($T_b = 34 \, ^\circ$C) and HFE-7100 ($T_b = 61 \, ^\circ$C). The findings were that:

- As the droplets approach the upstream surface of the cylinder, they bent away and little of the water (< 5 %) impacted the surfaces and dripped into the collector.

- The concentration of droplets behind the cylinder was significantly reduced from the upstream value.

- Many impinging droplets rebounded off of the surface and into the free stream. As expected, there was no evidence of secondary breakup of the droplets.

- Fine droplets were preferentially entrained into the recirculation region behind the cylinder while the larger droplets impacted the cylinder surface, accumulated and dripped off, and/or rebounded and dispersed radially outward into the free stream.

- When the cylinder was heated, droplet vaporization at the surface did not result in the complete removal of the smaller size droplets from the distribution, but rather decreased the size of all droplets.

- Droplet size increased and velocity decreased with increasing agent boiling point (Figure 2); the differences for the two HFEs are small but real. The HFE droplets with their lower boiling points vaporized even before reaching the obstacle surface.

**Figure 2A. Comparison of the Droplet Mean Size for Three Agents (The flow direction is from right to left.)**
We have now demonstrated that VULCAN simulations are capable of reproducing observed behavior of a gas phase suppressant with a single clutter object. The behavior is shown in Figure 3. Case A1 compares well with the experimental measurements of flames stabilized behind an obstruction in a laboratory wind tunnel (Figure 4).\(^4\) We then investigated the effect of a second clutter element on the suppression of fires stabilized behind a primary clutter object. The second element was situated to affect the flow patterns but not directly stabilize the flame. Nonetheless, the aerodynamic drag on the secondary clutter can create high and low pressure regions on the leading and trailing sides of the clutter. For high-pressure regions located adjacent to flame-stabilizing recirculation zones (Figure 4, Case A5), mixing of suppressant into the stabilization region is substantially enhanced, leading to reduced suppressant requirements. Conversely, if the low-pressure region is adjacent to the flame-stabilizing recirculation zones (Figure 4, Case A3), mixing of suppressant into the stabilization region is inhibited, leading to slightly greater suppressant requirements.

Figure 3. Fires Stabilized Behind a Backward-Facing Step in a Square Wind Tunnel. [The hot colors represent the flame, purple is the JP-8 pool, blue is the inlet and gray represents the structure, less the left wall and top surface that have been removed for visibility.]
VULCAN simulations are also being conducted to identify conditions for which suppression of a pool fire will and will not be successful in a ground-based F-18 E/F engine nacelle simulator. A four-nozzle design leads to good suppressant distribution (in the absence of a fire) over the expected range of operating conditions. In order to create conditions for which fires will not be suppressed, we have capped each of the nozzles in turn. Figure 5 indicates that capping nozzle 2 has the most dramatic effect, leaving a substantial fraction of the nacelle volume with insufficient suppressant to extinguish a fire. The lack of suppressant is most severe along the lower nacelle regions where pool fires would exist. Interestingly, Figure 5 also indicates that capping nozzle 3 has a minimal effect on the suppressant distribution. Suppressant dispensed from nozzle 3 tends to overlap in space with the suppressant dispensed from other nozzles. Thus, the outcome of an experiment with nozzle 3 capped will be instructive.

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4. Enhanced Powder Panels for Dry Bay Fire Protection

The NGP has completed its research into enhanced powder panels with both success and high visibility. These aircraft fire protection devices, attached to flammable fluid containers adjacent to dry bays, provide passive, lightweight, effective fire protection against ballistic impact. The new designs have a 60 % reduction of weight (to an areal density as low as 0.136 g/cm²) and thickness (to as low as 1.65 mm) over our prior designs. These are 30 % lighter and 40 % thinner than conventional commercial panels, yet they release as much as 21 times more powder mass or 42 times greater percentage of total powder. Much of this was due to an innovative overall panel design that maximizes its front face fracture relative to commercial powder panels. These advanced panels were calculated to be lighter than other active dry bay fire extinguishing systems and current commercial powder panels for two diverse dry bay applications.

Live fire demonstration tests of the optimized enhanced powder panels were conducted in a 0.45 m³ dry bay and fuel tank containing at least 49 L of JP-8. Nine tests were conducted with 12.7 mm armor piercing incendiary projectiles fired at a velocity of approximately 757 m/s. Figure 6A shows the commercial powder panel following a test that resulted in fire ignition, although the panel dislodged from the fuel tank during the impact event. Figures 6B and 6C show two different enhanced powder panel designs. Four of the six enhanced powder panel tests resulted in prevention of fire ignition. One of the other two tests resulted in the extinguishment of a fire 0.28 s after impact; however, it was most likely caused by the ignition of a pool of residual fluid.
from a previous fuel tank leak. The sixth test also resulted in fire ignition, but as in the commercial panel test, the panel dislodged from the fuel tank due to an ineffective adhesive. Powder dispersion was evident throughout the dry bay following enhanced powder panel tests and remained dispersed for at least five minutes or more in most tests as can be seen by observing the left side of the "dry bay" in Figure 6D.

Figure 6. Photographs Following Live Fire Demonstration Tests

A. Commercial Powder Panel

B. Enhanced Design 1

C. Enhanced Design 2

D. Enhanced Design 2

WHAT LIES AHEAD?

As the NGP approaches the meeting of its goal, the research will be focusing on two technical components:

- Evaluating the “world of chemistry” for new flame suppression chemicals that are operable in aircraft dry bays and engine nacelles. It is essential that as many candidates as possible are identified and screened as potential halon 1301 alternatives. It is equally
important that chemical families with no potential be so designated, along with the reasons for the designation. Thus, for other applications or should suppressant requirements change for fire suppression in aircraft, future investigators will have the benefit of the current program findings.

- Developing principles for optimizing suppressant storage and delivery. Both research and engineering experimentation have shown that there is much system effectiveness to be gained if the suppressant is deployed efficiently and much to be lost for a delivery design that is incompatible with the suppressant properties.

As these efforts near completion, a modest series of real-scale fire suppression tests will be conducted with the purpose of demonstrating the validity of the above findings.

**RECENT PUBLICATIONS**

**New Flame Suppression Chemistry**


**Improved Suppressant Delivery**


