ADVANCED PROPELLANT/ADDITIVE DEVELOPMENT FOR FIRE SUPPRESSING GAS GENERATORS: HYBRID SYSTEMS

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ABSTRACT

The "Advanced Propellant/Additive Development for Gas Generators" project is a collaborative effort between General Dynamics OTS-Aerospace (GD), Redmond, WA and the Naval Air Warfare Center-Weapons Division (NAWCWD), China Lake, CA. The project objective is to develop highly efficient, environmentally acceptable, chemically active fire suppressant capabilities based upon solid propellant gas generators, and to improve the understanding of propellant and additive effectiveness in fire suppression through testing. This paper reports on two segments: (1) development of cool burning propellant formulations and (2) fire testing of chemically active agents within the Solid Propellant Gas Generator (SPGG) and Hybrid Fire Extinguisher (HFE) configurations. Propellant formulations in development contain 5-aminotetrazole and the new high nitrogen compound BTATZ ($C_4H_4N_{14}$). These fuels are being refined to reduce overall combustion temperatures while maintaining ballistic robustness.

Fire testing conducted using chemically active agents (potassium iodide and potassium carbonate) demonstrated a >50% improvement in effectiveness when tested parallel to inerting systems. Similar performances were also observed between SPGG and HFE gas generator devices on a total inerting agent load basis. Fire testing was conducted at the GD facility in the Fire Test Fixture (FTF) against a controlled JP-8 fire. This paper summarizes the results to date of propellant formulation development, chemically active agent performance in a tire scenario, and HFE versus SPGG effectiveness.

INTRODUCTION

A proven approach to nonhalon fire suppression is based upon technology used in automobile airbag devices, whereby the fire suppression agent is a mixture of inert gases stored not in pressurized bottles but in the form of solid propellants [1, 2, 3]. Upon combustion in an **SPGG,** the solid propellant rapidly produces large quantities of inert gases such as nitrogen, carbon dioxide, and water vapor; these gases can be directed into a fire-containing volume at quantities sufficient to suppress combustion. The compact nature of the **SPGG** device makes it a volumetrically efficient means for chemically "storing" gaseous agents in a solid form.

SPGGs can also be used in conjunction with alternative fire suppression fluids such as fluorocarbons or water, in what is generally called an HFE. In an HFE configuration, the gas produced by the **SPGG** (a) pressurizes and (b) mixes with the "hybrid fluid." The **SPGG** therefore eliminates the need to store a pressurized fluid, thereby decreasing volumetric requirements, and also provides a means for more rapid distribution of the agent. As an added benefit, the hybrid fluid cools the exhaust of the **SPGG.**

The radical scavenging capability of Halon 1301 makes it a much more efficient fire suppressant than most of its replacement candidates, which tend to be chemically inactive, physically acting suppressants. Recent work has characterized the nature of different chemically active species, including halogen, and metallic and non-metallic species, in the fire suppression process [4]. Several workers point to the synergy that derives from combining chemical activity with physical (cooling, dilution) suppression processes [5]. Earlier work by GD/NAWC [1] has demonstrated the improvements possible by incorporating chemically active precursors into the **SPGG** event. This present work describes the benefits achievable by incorporating the chemically active additive directly into the propellant and/or hybrid fluid.

SPGG and HFE approaches to fire suppression have been developed and demonstrated in full-scale testing by GD in a variety of vehicle platforms, including military aircraft drybays and engine bays, military land vehicle engine and crew compartments, and commercial automobile engine compartments [1].

In this project, the GD/NAWC team has developed propellant compositions that provide significant improvements in fire protection performance. These developments have resulted in cooler, more efficient and more compact fire suppression agent systems. These accomplishments are made possible by taking advantage of the great flexibility of solid propellant technology.

RESULTS

PROPELLANT DEVELOPMENT: COOLER FORMULATIONS

Initial efforts on the GDMAWC-WD, NGP effort have considered propellant modifications that can be readily compared with the GD FS01-40 chemically inert solid propellant formulation. The formulations studied on the NGP program have thus far attempted to both reduce combustion temperatures—by increased levels of nitrogen generation and coolant addition—and incorporate additives to provide some amount of chemical activity to the propellant exhaust. Propellant formulations incorporating the new high nitrogen compound BTATZ ($C_4H_4N_{14}$), while structurally similar to the 5-aminotetrazole (SAT) fuel used in the GD FS01-40 propellant (Figure l), appear to provide increased means for reducing propellant combustion temperatures.

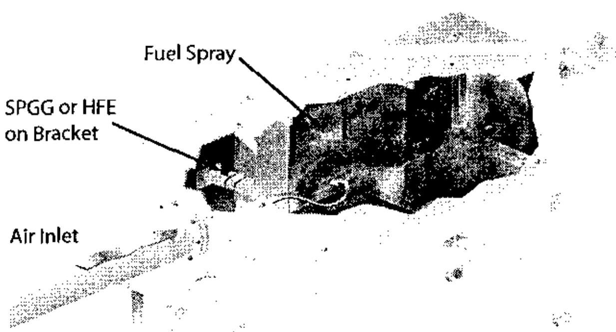

Figure 1. GD Fire Test Fixture (FTF).

The preparation of BTATZ has progressed to the 1 lb scale. ***On*** this scale the material is more difficult to purify in that extensive solvent extraction is required to remove the small amount of impurities present. This may not be significant in the long run **as > 97%** purity is easily achieved without extensive purification (i.e., **97%** pure material maybe sufficient). The final purity of BTATZ is generally **> 99%** on smaller scale experiments and is also achievable on the 1 lb scale with extra purification. **Our** synthesis of BTATZ so far has used intermediates provided by Los Alamos National Laboratory (LANL). These materials have been exhausted and will now have to be synthesized in-house. **Work** on the 3 gal. scale has proven successful. The recent acquisition of a 50 gal. reactor will facilitate project scale-up to such an extent that the synthesis of intermediates need only be carried out periodically.

Further safety data on BTATZ itself has been obtained. BTATZ shows acceptable friction and impact sensitivity but is somewhat sensitive to electrostatic initiation. When formulated into **a** molding powder with poly(ethyl acrylate) (3% as a binder), electrostatic sensitivity is still a concern, even when 0.5% carbon black is added; however, when pressed into pellets or deposited as a thin layer, the material meets the criteria set for routine handling of energetics.

Initial ballistic characterization of material prepared at NAWCWD indicates similar performance to the BTATZ prepared at LANL. A number of formulations are currently under ballistic evaluation. NAWC-WD has made progress on bum rate measurements for formulations based on the new high nitrogen compound BTATZ($C_4H_4N_{14}$). The results are presented in Table 1.

TABLE 1. BTATZ-PROPELLANT PROPERTIES.

Formulation	5-AT	BTATZ[a]	Oxidizer	0 psi	500 psi	1000 psi	1750 psi	2500 psi	n
1		97		0.25	1.75	2.14	2.64	3.62	0.51
2	48	48			0.18	0.55	1.18	1.66	1.4
3	24	72			1.57	1.78	2.63	3.44	0.71[b]
4	43	43	10($KClO_4$)	-	0.34	1.31	2.07	2.46	
5	43	43	10(KNO_3)	-	0.14	0.61	1.03	2.00	1.6
6[d]	-	86	10(KNO_3)	0.18	1.29	2.15	2.46/2.62	3.03	0.55
7[d]	-	86	10($KClO_4$)	0.16	1.12	1.80	2.38/2.66	3.11	0.57

[a] The balance remaining in each formulation is made up of binder, opacifier, and process aid.
[b] Linear over 1000 – 2750 psi; n is lower below 1000psi.
[c] Non-linear: approximately 0.5 (1750–2500 psi), decreasing at lower pressures.
[d] Measurements at 1500 and 2000 psi.

Over the range 1750-2500 psi, the pressure exponent for formulation 4 is 0.5 and decreasing. This formulation, a promising candidate as the bum rate, is relatively high at low pressures and has a decreasing pressure dependence of the bum rate. Formulations 6 and 7 also exhibit ideal ballistics for gas generator applications with pressure exponents around 0.5 and with relatively high bum rates. Future work includes suppression testing with Formulations 4-6 and modifications thereof.

ADDITIVE DEVELOPMENT: ACTIVE COMPOSITIONS

SPGG technology enables chemically active agents to be stored and generated synergistically with inerting or cooling agents. Combustion of the solid propellant produces inert or cooled gases; the chemically active agent is liberated and entrained in the discharge. HFE technology introduces additional capabilities, whereby chemically active agents may be integrated into the gas generator solid propellant or hybrid liquid. Chemically active additives tested in the course of this project include various alkali halides (e.g., KBr, KI), alkali carbonates (e.g., K_2CO_3) and polyhalogenated aromatics (pentabromophenyl ether). Three different approaches were evaluated for incorporation of chemically active additives into suppressant exhaust: (1) blend the additive (or a precursor) directly into the propellant for SPGG delivery; (2) use a chemically active propellant formulation with an inert hybrid fluid for HFE delivery; and (3) blend the additive (or a precursor) directly into the hybrid fluid for HFE delivery. Delivery approaches 1-3 were assessed by testing on a single common test platform using as hybrid fluid HFC-227.

FIRE EFFECTIVENESS TESTING: TEST FIXTURE

Fire suppression effectiveness testing was undertaken using a mid-scale FTF, developed by GD to simulate typical military aircraft fire scenarios (e.g., [4]). Gas generator fire suppression devices were used to deliver both inert and active agents into the fire. Operational parameters for the GD FTF are given in Table 2; the fixture is illustrated in Figure 2. The test fixture operates with an air to fuel mass ratio of about 31, giving the fire an intensity of about 1 MW. This was derived by using a fuel heating value of 46.4 MJ/kg for JP-8 fuel and a fuel flow rate of about 0.03 lbm/sec (15 g/sec).

Instrumentation was installed in the test fixture to monitor and control test variables, and to make sure they stay in similar ranges from test to test. The gas generator devices were fired and the agent discharged after a steady-state fire was established. A waiting period of 30 sec between JP-8 fire ignition and gas generator device firing was kept to ensure steady-state, repeatable test conditions. The gas generator device was located in the forward chamber of the FTF (upstream of the fire). The gas generator device was mounted on an arm in the middle of the airflow, but shielded from the fire zone by a baffle. Figure 2 illustrates the gas generator device placement in the FTF. All GPGG and HFE discharge times were maintained at –200 ms for ease of comparison.

TABLE 2. FIRE TEST FIXTURE PARAMETERS.

Airflow		
Mass flow rate	454 g/s	1.0 lbm/s
Volumetric flow rate	385 L/s	13.6 ft^3/s
Linear Fflow rate (in pipe)	762 *cmls*	*25* ft/s
Fuel Flow		
Fuel	**JP-8**	
Mass flow rate	15 g/s	0.033 lbm/s
Volumetric flow rate	19 ml/s	0.005 gal/s
Stoichiometry		
Air-fuel ratio $(\dot{m}_{air}/\dot{m}_{fuel})$	31	
Equivalence ratio	0.50	
Fire Zone Dimensions		
Flame temperature	1000 K	1300°F
Intensity	700 kW	700 kW
Length	122 cm	**4ii**
Cross-sectional area	3700 cm^2	4 ft^2
Volume	450 L	**16 ft^3**
Residence time	1.2 s	***1.2*** s
Injection interval	–100-200 ms	–100-200 ms

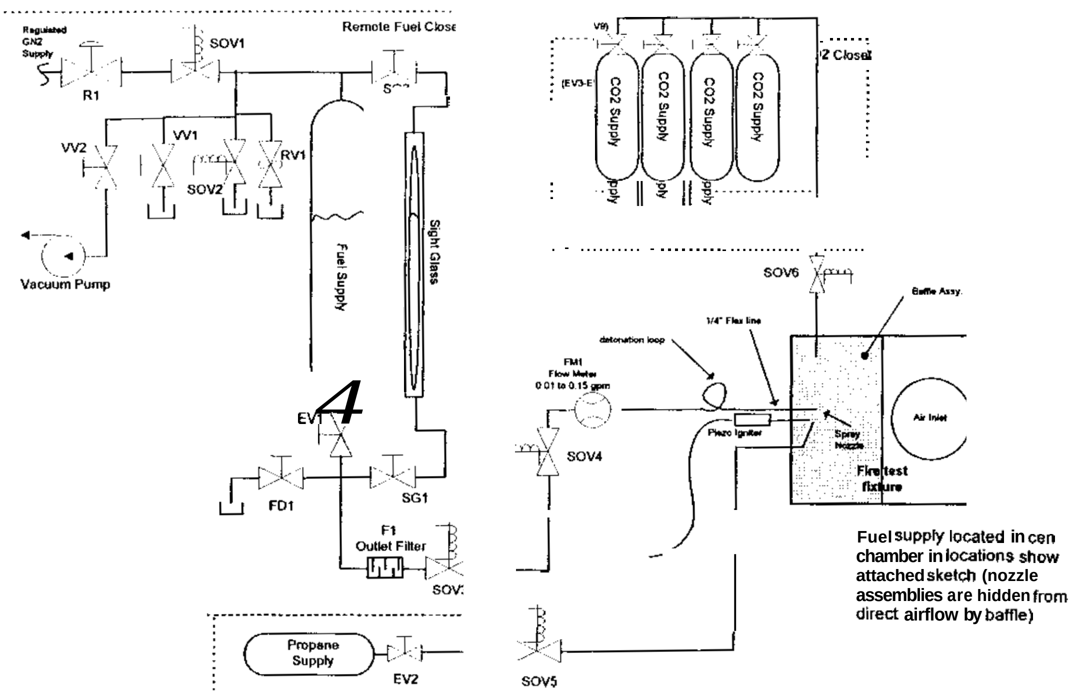

Figure *2*. FTF test facility schematic.

The FTF test facility consists of the following major subsystems:

- Main test chamber
- Airsupply
- Fuel supply
- Ignition system
- Suppression device
- CO, emergency extinguishing
- Control and data acquisition

FIRE EFFECTIVENESS TESTING: GAS GENERATOR AND HYBRID FIRE SUPPRESSION DEVICES

The gas generator devices used in this testing consist of (1) a Solid Propellant Gas Generator (SPGG) (Figure **3)**, and (2) a Hybrid Fire Extinguisher (HFE) (Figure 4). SPGG technology rapidly produces large quantities of inert gases such as nitrogen, carbon dioxide, and water vapor to suppress combustion. HFE technology combines a solid propellant gas generator with a fire suppressing fluid, e.g., HFC-227, to provide fire suppression capabilities similar to the SPGG. Chemically active additives were incorporated into the solid propellant for both the SPGG and HFE devices and also into the hybrid fluid for the HFE.

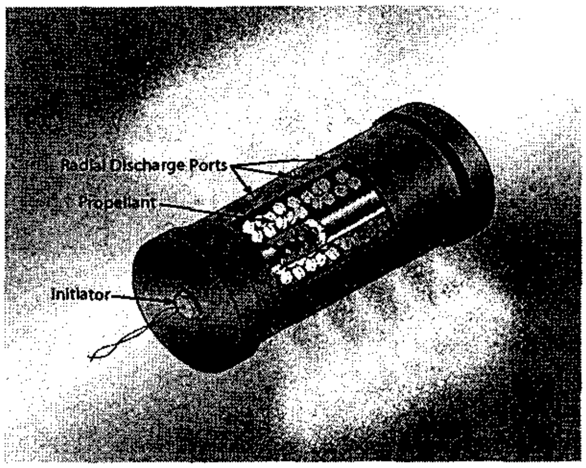

Figure **3.** SPGG.

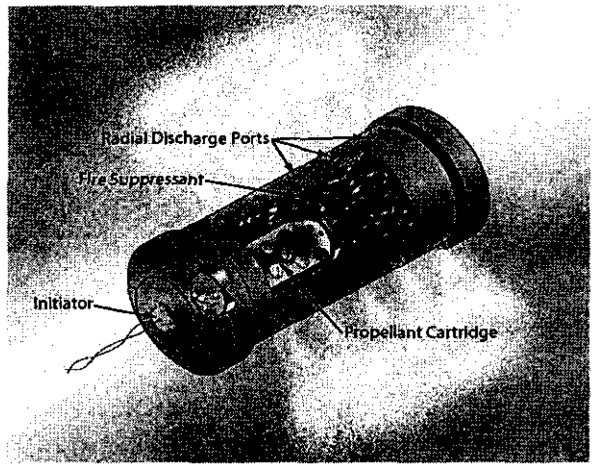

Figure 4. HFE.

Chemically inert and active agents were tested in the FTF to evaluate their effectiveness in fire suppression. The GD FSOI-40 propellant generates an inert blend of CO_2, N_2, and H_2O when functioned. Two active agents were evaluated, as incorporated into the FS01-40; these agents were KI and K_2CO_3. HFC-227 was used as the hybrid fluid during all of the tests conducted with HFE devices. Chemically active agents were incorporated into the HFE devices by using either chemically active propellant formulations to pressurize and disperse the HFC-227, or inert FS01-40 to pressurize and disperse a mixture of active agent powder mixed in the hybrid fluid HFC-227. The two active agents mixed with HFC-227 during HFE testing were $KHCO_3$ and $NaHCO_3$. Agent effectiveness was evaluated in terms of several measures, including total agent mass required for flame extinction and a normalized FSN value (=agent threshold loading/(threshold load for **GD's** FS01-40 SPGG)). The flow-rate adjusted mass fraction of agent, β, was also used; this is defined **[6]** as

$$\beta = \frac{\dot{m}_{agent}}{\dot{m}_{air} + \dot{m}_{agent}}$$

where $\dot{m}_{agent}$ and $\dot{m}_{air}$ are the agent and air mass flow rates respectively. The critical mole fraction Xc was obtained from β by adjusting for (inert) agent molecular weight,

$$X_c = \frac{\beta / MW_{agent}}{(\beta / MW_{agent}) + ((1-\beta)/MW_{air})}$$

FIRE EFFECTIVENESS TESTING: SPGG FIRE TEST RESULTS

Chemically active agents were vaporized during propellant combustion and delivered into the fire zone by high-temperature exhaust gases from a solid propellant gas generator producing a blend of CO_2, N_2, and H_2O. The results of SPGG testing are summarized in Table **3;** the values are based on multiple tests

TABLE 3. SPGG FTF **DATA SUMMARY.**

Agent	FS01-40	GD-02	GD-04
Active additive	—	KI	K_2CO_3
Gas fraction	50%	50%	50%
MW, *glmole*	30	30	30
Mole active (K)/100g	0	0.127	0.145
GG Load	347	I57	IOS
Discharge time, ms	200	200	200
Discharge mass, g	173.5	78.5	52.5
Mole active (K) discharged	0	0.199	0.152
m•(agent), g/s	868	393	263
FSN(FS0 **1-40)**	I	0.452	0.303
Beta	0.656	0.464	0.366
Critical mole fraction	0.649	0.455	0.359

and represent the threshold amount of agent needed to extinguish the fire. Typically, three tests were conducted at the threshold amount, and three additional tests were conducted at an agent load greater than the threshold amount. The threshold is defined **as** the amount of agent needed to extinguish the fire at least two out of three times.

The test results indicate that K_2CO_3 and KI yield significantly improved suppression effectiveness when compared to the inert propellant compositions. For a composition containing 0.1 moles KI per 100 grams propellant, the threshold propellant load was ~ 45% that of FS01-40, with similar discharge conditions and **mass** flow rates. **A** composition containing a similar amount of K_2CO_3 (0.1 moles K per 100 grams propellant), resulted in threshold loads of 0.3x FS01-40.

FIRE EFFECTIVENESS TESTING: HFE FIRE TEST RESULTS

The results of **HFE** testing are summarized in Table 4, which lists threshold amounts. The threshold is defined as the agent load needed to extinguish the fire two out of three times. FTF testing with inert and chemically active hybrid (HFE) configurations mirror the enhanced efficiency seen in the SPGGs.

TABLE 4. HFE FTF **DATA SUMMARY.**

Agent	FS01-40/ HFC-227	GD-021 HFC-227	GD-04/ HFC-227	FS01-40/HFC-227 KHCO,
Active additive	—	KI	K_2CO_3	KHCO,
Gas fraction	95%	95%	95%	95%
MW, glmol	170	170	170	170
Mole active (K) /100g	0	0.127	0.145	0.145
GG Load	358	228	228	265
Discharge mass, g	340.1	216.6	216.6	252
Mole (K) discharged	0	0.040	0.046	0.052
Discharge time, ms	200	200	200	200
m•(agent), g/s	1701	1083	1083	1260
m•(air), g/s	454	454	454	454
Beta	0.789	0.705	0.705	0.735
FSN(FS01-40)	1.960	1.248	1.248	1.452
Critical mole fraction	0.430	0.324	0.324	0.321

The test results again indicate that KI and K_2CO_3 yield significantly improved suppression effectiveness when compared to the inert propellant compositions. Results also indicate that an active additive in the hybrid fluid yields significantly improved suppression effectiveness.

DISCUSSION

Propellant formulations incorporating the new high nitrogen compound BTATZ ($C_4H_4N_{14}$), while structurally similar to the 5-aminotetrazole (5AT) fuel used in the **GD** FS01-40 propellant, appear to provide increased means for reducing propellant combustion temperatures. The preparation of BTATZ has progressed to the 1 lb scale. This increased production capability plus the attractive ballistic (burn rate, pressure sensitivity) of BTATZ formulations make them ideal candidates for future work, including reformulation with additional chemical coolants as well as SPGG suppression testing.

Figure 5 summarizes the test results and shows how the test configurations compare on a total agent weight basis and also on a K-molar basis. FTF testing with various inert and chemically active solid propellant compositions demonstrates that incorporation of 0.1 mole % additive into inert fire suppressants can have a dramatic effect upon suppression efficiency. The otherwise similar propellant compositions examined during this testing indicated a 50-70% reduction (by mass) of agent loading for suppression of identical **fires** when the propellant composition contained as little as 0.1 mole % (expressed as a fraction of the gaseous output). On an equimolar basis, potassium carbonate appears to be a more effective chemical additive than potassium iodide.

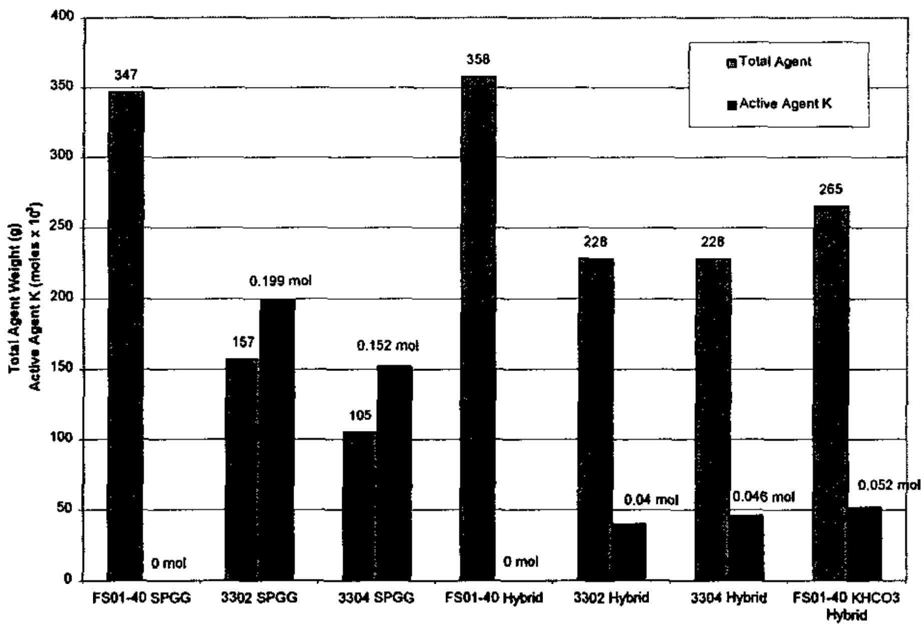

Figure 5. Total agent weight needed to extinguish fire.

The greater effectiveness of potassium carbonate is consistent with previous testing, both on the present test fixture as well as turbulent spray burner testing [1]. One possible explanation for this trend includes more fascile vaporization of the chemically relevant potassium species from the K_2CO_3. Although this is inconsistent with the higher melting point of K_2CO_3 vs KI (**891** "C vs **681** °C), respectively, it may be consistent at higher temperatures where K_2CO_3 decomposes before boiling whereas KI melts without decomposition at 1330 "C. Another possibility is that there is an antagonistic interaction between the halogen and alkali metal species in the flame region. Similar findings have been reported by Linteris et al. [7] for premixed flames with ferrocene/iron pentacarbonyl species in the presence of fluorocarbons.

On a mass-to-mass basis, the inert HFE and SPGG systems appear to provide similar suppression protection, requiring - 360 grams to suppress the 1 MW GD FTF fire. The higher molar efficiency of the hybrid testing reflects the higher molecular weight of the HFC-227. As in the SPGG case, incorporation of chemically active species into the propellant improves the suppression efficiency for the HFE configuration. Testing conducted with KHCO, added to the hybrid fluid of the HFE system produced results similar (based on moles of **K)** to those with active agents (KI, K_2CO_3) added to the propellant, which indicates that active additives in the hybrid fluid may be just **as** effective **as** active additives in the propellant.

The improvement found for the HFE systems appears to be less than that found in the SPGGs, i.e., an approximate 30% reduction in suppressant mass. Note, however, that the propellant is 100% of the total agent weight for the SPGG configuration, but only 14% of the total agent weight for the HFE configuration, thus limiting the molar fraction of chemically active additive to **~2** mole %. It is likely that if the amount of active additive in the HFE systems were optimized, these systems would show a weight reduction similar to the SPGG systems.

The flow-rate adjusted **mass** fraction of agent, β, for these tests is higher than reported in other reports of baffle-stabilized flames ***[6,*** 8]. However, those reports show that β as well as the critical mole fraction increases at shorter discharge times. This is consistent with the need for high agent concentrations in the free stream in order to achieve sufficient mixing of the agent into the flame recirculation zone and thereby achieve concentrations sufficient to effect extinction. Future work will address the correlation of discharge times and mass flow rate effects.

SUMMARY

Propellant formulations incorporating the new high nitrogen compound BTATZ ($C_4H_4N_{14}$) appear *to* provide increased means for reducing propellant combustion temperatures. The preparation of BTATZ has progressed to the 1 lb scale. This increased production capability **plus** the attractive ballistic (burn rate, pressure sensitivity) of BTATZ formulations make them ideal candidates for future work, including re-formulati011with additional chemical coolants **as** well as SPGG suppression testing. Testing of propellant compositions containing potassium iodide and potassium carbonate **as** chemically active additives demonstrated enhanced effectiveness in fire scenarios as compared to chemically "inert" compositions. These new propellant formulations are lighter in weight than Halon 1301 for comparable fire suppression effectiveness, and the hazards associated with halon's ozone depletion capability are not present.

FTF testing with various inert and chemically active solid propellant compositions demonstrates that incorporation of 0.1 mole % additive into inert fire suppressants can have a dramatic effect upon suppression efficiency. The otherwise similar propellant compositions examined during this testing indicated a 50-70% reduction (by mass) of agent loading for suppression. On an equimolar basis, potassium carbonate appears to be a more effective chemical additive than potassium iodide. The greater effectiveness of potassium carbonate (vs. potassium iodide) is not yet well understood, but may be related to more fascile vaporization of the carbonate-based species after melting, or to an antagonistic interaction between the halogen and alkali metal species in the flame region.

On a mass-to-mass basis, the inert HFE and SPGG systems appear to provide similar suppression protection. Incorporation of chemically active species into the HFE propellant improves the suppression efficiency for the HFE configuration. Testing conducted with additives incorporated into the hybrid fluid of the HFE system produced results similar to those achieved with active agents added into the propellant. This indicates that active additives in the hybrid fluid may be just **as** effective **as** active additives in the propellant.

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REFERENCES

1. Fallis, **S.,** Reed, R., Lu, Y-C,. Wierenga, P.H., and Holland, G.F., "Advanced Propellant/Additive Development for Fire Suppressing Gas Generator," Proceedings, Halon Options Technical Working Conference, Albuquerque, NM, pp. 361-370, 2000.
2. Neidert, J.B., Black, R.E. III, Lynch, R.D., Martin, J.D., and Simpson, T., "Fighting Fire with Fire: Solid propellant Gas Generator Technology for Fire Suppression," *JANNAF* Propulsion Meeting, Vol. II, Cleveland, OH, pp. ***77-86,*** 1998.
3. Hamins, A., Cleary, T., and Yang, J., "An Analysis of the Wright Patterson Full-scale Engine Nacelle Fire Suppression Experiments," NISTIR-6 193, National Institute of Standards and Technology, Gaithersburg, MD, 1997.
4. Babushok, V., Tsang W., Linteris, G.T., and Reinelt, D., "Chemical Limits to Flame Inhibition," Combustion *and Flame*, 115, pp. 551-560, 1998.
5. Noto, T., Babushok, V., Hamins, A., and Tsang, W., "Inhibition Effectiveness of Halogenated Compounds," Combustion *and Flame*, 112, pp. 147-160, 1998.
6. Hamins, A., Presser, C., and Melton, L., "Suppression of a Baffle-Stabilized Spray Flame by Halogenated Agents," Twenty-Sixth *Symp.* (International) ***on*** Combustion, pp. 1413–1420, 1996.
7. Linteris, G.T., and Rumminger, M.C., "Premixed Carbon Monoxide/Nitrous Oxide/Hydrogen Flames: Measured and Calculated Burning Velocities With and Without $Fe(CO)_5$," *Combustion* and Flame, 122, pp. 58–75, 2000.
8. Takahashi, F., Schmoll, W.J., Strader, E.A, and Belovich, V.M., "Suppression of Nonpremixed Flame by a Backward Facing Step," Combustion *and Flame*, 122, pp. 105–116, 2000.