ADVANCED PROPELLANT/ADDITIVE DEVELOPMENT
FOR FIRE SUPPRESSING GAS GENERATORS

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INTRODUCTION

Most replacement candidates for Halon 1301 are fluorocarbon agents like HFC-125 (C_2HF_5) and HFC-227 (or FM-200, C_3HF_7) [1]. The absence of heavy halogen atoms (e.g., Cl, Br, or I) make these agents primarily physically acting suppression agents, functioning through cooling and dilution effects [2]. As such, these replacement agents are much less efficient that Halon 1301 and so require greater concentrations to attain the same effectiveness.

A proven approach to nonhalon fire suppression is based upon technology similar to that used in automobile airbag devices. In this approach, the fire suppression agent is a mixture of inert gases, which are stored not in pressure bottles but in the form of solid propellants [3, 4]. On combustion in a solid propellant gas generator (SPGG), the solid propellant produces large quantities of inert gases such as nitrogen, carbon dioxide, and water vapor. The compact nature of the SPGG device makes it a remarkably efficient means for chemically storing gaseous agents in a solid form. Early developments of this approach were pioneered at NAWC-China Lake in 1986 [5] and later refined [6] and demonstrated in full-scale testing by PAC 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 [4].

The current state of the art SPGG fire suppression system — PAC FS01-40 — is competitive in size with Halon 1301 systems on both mass and volume bases. It is clean, effective, and fast acting, environmentally rugged and reliable, nontoxic, and SNAP approved. Current products are based on commercial automotive airbag technology, thereby providing for a smooth transition from military to commercial applications.

A class of "superagents" has long been known, which exhibit fire suppression effectiveness much greater than Halon 1301 [7]. Although the foremost example of these agents is iron pentacarbonyl, $Fe(CO)_5$, other examples include chromyl chloride, CrO_2Cl_2, and tetraethyl lead, $Pb(C_2H_5)_4$, as well as powdered materials such as $K_3Fe(CN)_6$. While effective, these superagents are highly toxic, and so are not used in general suppression applications. However, much insight into the mechanism of chemically active fire suppression has been gleaned by a study of the chemical kinetics associated with the action of these superagents upon hydrocarbon combustion [8, 9]. For instance, chemical kinetic modeling of "superagent" suppressants indicates that the $Fe(CO)_5$-based scavengers. or iron oxide species, such as FeO and FeOH, are more effective than halogens (e.g., I•, Br•) in flame suppression, because they are more easily regenerated. The key to the effectiveness of iron pentacarbonyl is the gas phase iron-oxo chemistry.

Next-generation SPGG fire suppression systems will capitalize upon the current technology and further enhance performance by using chemically active additives such as found in "superagent" sysems. SPGG technology provides an extremely flexible agent platform whereby one can readily incorporate additives that can be converted into the high-performance metal-oxo species

of the superagents — without the associated toxicity risk [10]. These next generation systems are expected to provide a means to reduce agent loads by 2–5x compared to current baselines.

In this NGP project, the PAC/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

Initial efforts on the PAC/NAWCWD, China Lake NGP effort have considered propellant modifications that can be readily compared with the PAC FS01-40 chemically inert solid propellant formulation. The formulations studied on the NGP program have thus far attempted to reduce combustion temperatures by (1) increasing levels of nitrogen generation and coolant addition, and (2) incorporating additives to provide some amount of chemical activity to the propellant exhaust.

COOLED PROPELLANT FORMULATIONS

Improved cooling and more efficient agent generation have been accomplished via variations in the overall solid propellant composition. Different combinations of fuels and oxidizers have been modeled and tested; these results are summarized in Table 1. Several high-nitrogen fuels were considered (Figure 1). These additives increased the production of the inerting agent nitrogen. Several compositions have been designed to deliver agent at a very rapid rate; this rate can be tailored by the incorporation of endothermically acting chemical coolants.

One reduced combustion temperature formulation is based upon 5-amino tetrazole (5-AT) and potassium perchlorate (KP), with an elastomeric binder added to facilitate pressing of pellets and increase abrasion resistance. This formulation bums well at 1000 psi (BR1000 = 0.2 in/s), but is somewhat sensitive to combustion pressure (n=0.8); this sensitivity limits commercial use of the formulation.

A new high nitrogen compound BTATZ ($C_4H_4N_{14}$) (courtesy of Mike Hiskey, Los Alamos National Laboratory) is currently under evaluation. Initial results indicate that this compound burns well at low pressures, and the bum rate has a low dependence on pressure (slope = 0.2, to be confirmed). Impact, friction, and electrostatic sensitivity data have been obtained. We have included BTATZ in several formulations in combination with 5-AT in an attempt to increase efficiency of combustion while keeping oxidizer content to a minimum. A composition (with 10% KP has a very low dependence of bum rate on pressure, with calculated combustion temperature approximately 1700 K (2600 °F), and gas production efficiencies yield over 4 mol gas/ 100g, nearly 60% of which is N_2.

Other high nitrogen compounds [11], e.g., GAZT, BT, GBT and TAGN, were tested in formulations and in thermochemical calculations. At this level of added oxidizer and with no coolants, all of the formulations exhibited high combustion temperatures and very high bum rates. The fact that the bum rates were so high indicates that at a lower level of oxidizer (or by addition of

TABLE I. COOL, HIGH NITROGEN DEVELOPMENTAL PROPELLANT COMPOSITIONS.

Composition	Current SOA		5AT		5AT/BTATZ(1)		5AT/BTATZ(2)	
Exhaust species (vol% @ T_c)	N_2	45	N_2	57.1	N_2	66.4	N_2	61.4
	CO_2	35	H_2	35.4	H_2	32.1	H_2	30.2
	H_2O	20	CO	7.5			CO	8.5
			KCl(s)	5.3g			KCl(s)	5.3g
Tex, K (°F)	1000 (1400)		x74 (1113)		908 (1175)		967 (1281)	
Gas Output, mol/ 100g (mol/100cc)	2 (5)		4.41 (7.41)		4.14 (6.87)		4.01 (6.86)	
Pressure exponent, n	0.5		0.80		1.6 (500-1000psi)		0.7 (1000-2750 psi)	
BR_{1000}, in/s	0.5		0.17		0.55		1.31	
	GAZT		BT		GBT		TAGN	
Exhaust species (vol% @ T_c)	N_2	37.6	N_2	44.6	N_2	42.9	N_2	28.3
	H_2O	28.8	H_2O	15.0	H_2O	28.8	H_2O	40.6
	CO_2	15.5	CO_2	25.8	CO_2	20.1	CO_2	16.4
	CO	11.4	CO	6.6	CO	12.8	O_2	11.5
	KCl(s)	32.6g	KCl(s)	33.6g	KCl(s)	33.1g	KCl(s)	5.3g
Tex, K (°F)	1436 (2125)		1761 (2711)		1457 (2163)		1421 (2098)	
Gas Output, mol/ 100g (mol/100cc)	2.51 (4.99)		2.13 (4.28)		2.19 (4.40)		2.44 (4.86)	
Pressure exponent	ND		ND		ND		ND	
BR_{1000}, in/s	>2.5		>2.5		>2.5		>2.5	

an oxidizer that promotes cooler burning) combustion will be efficient in terms of nitrogen generation as well as burning cooler.

CHEMICALLY ACTIVE ADDITIVES

Fire suppression effectiveness of SPGG systems was also increased by incorporation of additives capable of interfering with and terminating radical processes associated with hydrocarbon combustion. Because the operational conditions *inside a* SPGG are similar to those in a fire, radical-trapping intermediates can be generated inside the GG and delivered with the inert gas coolant to the fire zone. Some 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 (pentabromo-phenyl ether). The physical properties of several chemically active suppressant compositions are summarized in Table 2.

Two different approaches were evaluated for incorporation of potassium into propellant exhaust: one begins with potassium nitrate, the other with potassium carbonate. Both formulations resulted in slightly reduced gaseous agent output when compared to an inert baseline composition, but had comparable ballistic characteristics. Likewise, iron oxide containing formulations exhibited viable rates of agent generation.
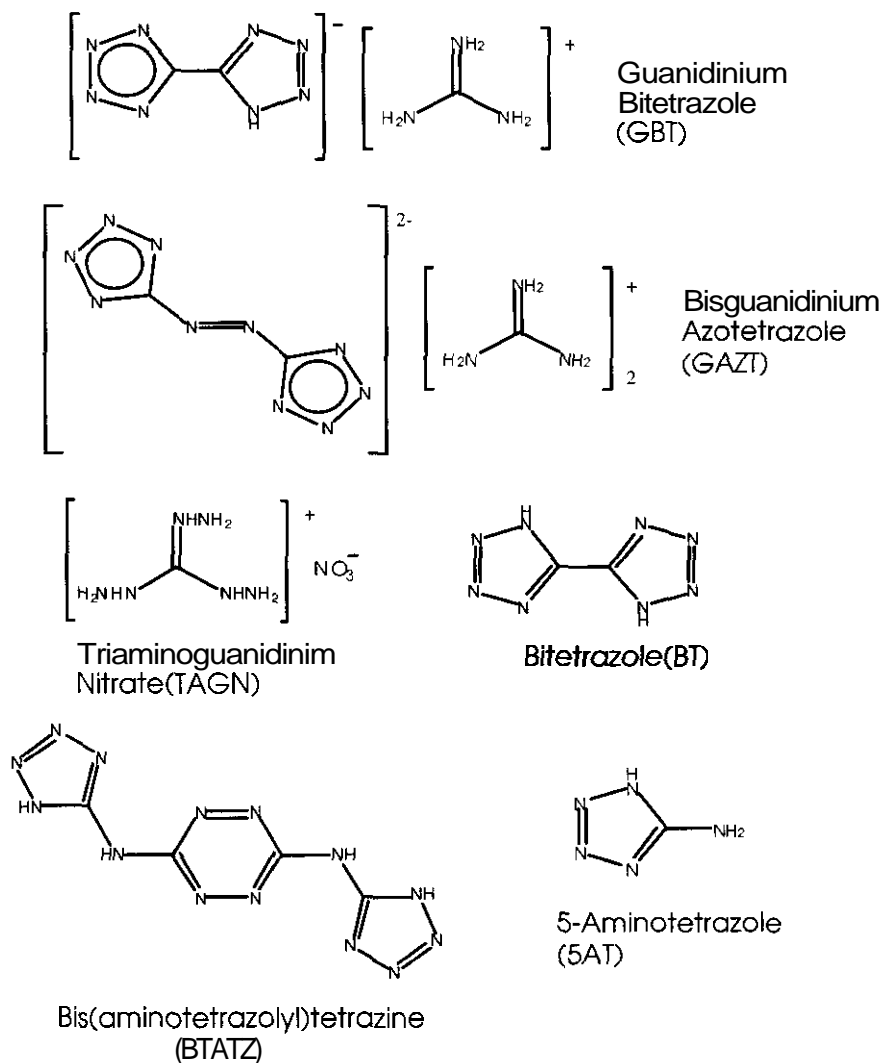
Figure 1. High-nitrogen fuels used in CL/PAC propellant development.

Propellant compositions were formulated both with and without pentalbromophenyl ether, added as a chemically active flame inhibitor, and underwent preliminary ballistic characterization. Larger pellets of the chemically active formulation were burned in a motor and the temperature of the gaseous products measured. The outlet (nozzle) temperature was approximately 675 °C, which was in good agreement with the temperature predicted from thermochemical calculations. The chemically active formulation was also found to be impact, friction, and electrostatically insensitive. Suppression effectiveness was demonstrated by directing the exhaust from propellant combusted in an Adam Motor into a 2 ft^3 vented box, where it successfully extinguished a JP-8 pool fire. UV camera data indicated that no H_2 burned during the discharge event.

SPGG AND FIRE EFFECTIVENESS TESTING

Fire suppression effectiveness testing was undertaken using a mid-scale Fire Test Fixture (FTF), developed by PAC and representative of typical military aircraft fire scenarios (e.g., [12]). Operational parameters for the PAC FTF are given in Table 3, with a drawing of the fixture in Figure 3.

TABLE 2. PROPERTIES OF CHEMICALLY ACTIVE DEVELOPMENTAL PROPELLANT COMPOSITIONS.

Composition	Current SOA		0807-Mod KN		0807-Mod K-Carh		0807-ModD		5AT/DECABr	
Exhaust species (vol% @ $T_,$, or g/100g propellant)	N_2	45	N_2	44.1	N_2	42.6	N_2	44	N_2	56.1
	$co2$	35	cor	35.2	CO_2	37.6	CO_2	36	H_2	34.0
	H_2O	20	H_2O	20.7	H_2O	19.9	H_2O	20	CO	7.8
			(K_2CO_3 9.0g)		(K_2CO_3 9.0g)		Fe_2O_3 5g		KCl(s) 20	
			(0.13 mol K)		(0.13 mol K)		(0.06 mol Fe)		KBr(s) 5.4g	
T_{ex}, K (°F)	1000 (1400)		1102 (1524)		1206 (1711)		1098 (1517)		874 (1113)	
Gas output, mol/100g (mol/100cc)	2 (5)		1.61		1.78 (4.09)		1.88 (4.87)		4.24 (7.29)	
Pressure exponent	0.5		0.66		0.59		0.62		1.0	
BR_{1000}, in/s	0.5		0.41		0.52		0.64		0.1	

TABLE 3. SUMMARY OF TEST FIXTURE PARAMETERS, PAC FIRE TEST FIXTURE.

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Airflow Rate	
Mass flow rate, m•, g/s (lbm/s)	384 (0.85)
Volumetric Flow Rate, L/s (ft^3/s)	316 (11)
Linear Flow Rate (in pipe), cm/s (ft/s)	670 (22)
Fuel Flow Rate	
Fuel	JP-X
Mass flow rate, m•, g/s (lbm/s)	20.23 (0.0446)
Volumetric flow rate, mL/s (gal/s)	25 (0.0661)
Stoichiometry	
m•$_{air}$/m•$_{fuel}$	19
Equivalence Ratio	
Fire Zone Dimensions	
T, K (°F)	1200 (1700)
Intensity, kW	1000
Length, cm	180
Cross-Sectional Area, cm^2	3700
Volume, L (ft^3)	670 (24)
Residence time, s	0.27
Injection Interval, ms	up to 8000
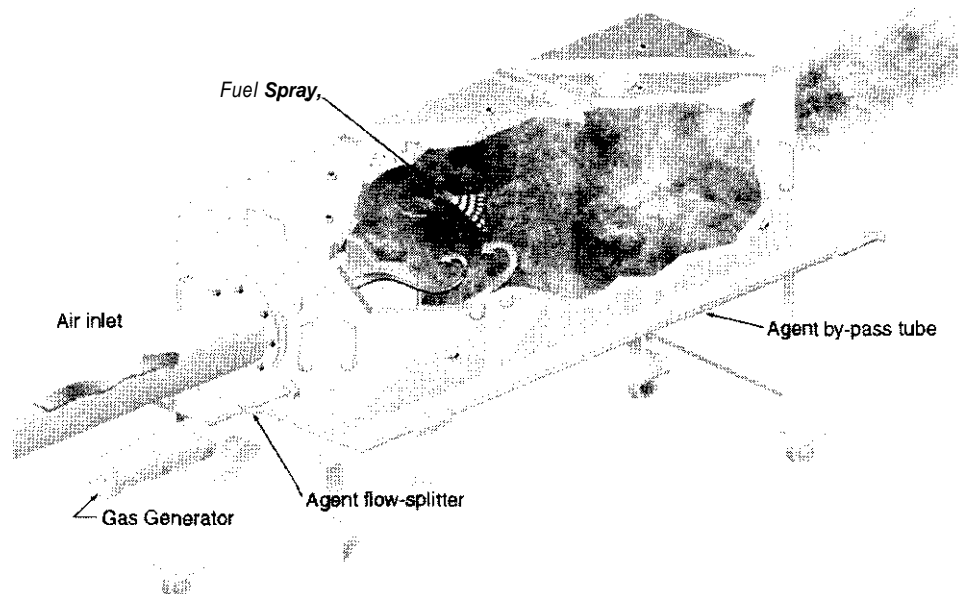
Figure 3. PAC Fire Test Fixture.

The fixture is located in a concrete reinforced test cell. The floor is painted with fuel-resistant, non-absorbing material. The test facility consists of several major subsystems including:

- Main Test Chamber
- Air Supply
- Fuel Supply
- Ignition

- Suppressant Discharge
- CO_2 Emergency Extinguishing
- Control and Data Acquisition

NGP FIRE TEST CONFIGURATION

For tests conducted under this program, the test fixture was usually operated at an air to fuel mass ratio of about 19. The fuel flow rate was about 0.04 lbm/sec (or 20 gm/sec). Using a fuel heating value of 46.4 MJ/kg, the fire intensity was about 1.0 MW.

Selected chemical agents were tested in the Fire Test Fixture to evaluate their effectiveness in fire suppression for the controlled JP-8 fire. The agents were loaded inside the discharge section of a neutral-burning, solid-propellant gas generator (SPGG) (Figure 4). The exhaust of SPGG consisted mainly of CO_2, N_2, and H_2O. During SPGG discharge, the chemical agents were supposed to be vaporized and delivered into the fire zone by the high-pressure and high-temperature exhaust gases. Fine-grid metallic meshes and porous plates were used downstream of the agents to enhance the mixing between SPGG exhaust and agents prior to entering the distribution tube.

The distribution tube was split into two lines, one enters the test fixture, and the other discharges directly to ambient (Figure 4). By varying the split ratio between these two lines, the amount of agent entering the fire zone can be controlled. In the tests, the split ratio was fixed to be 50%, and the initial agent quantity in the SPGG was varied. Thus, the objective of the tests was to
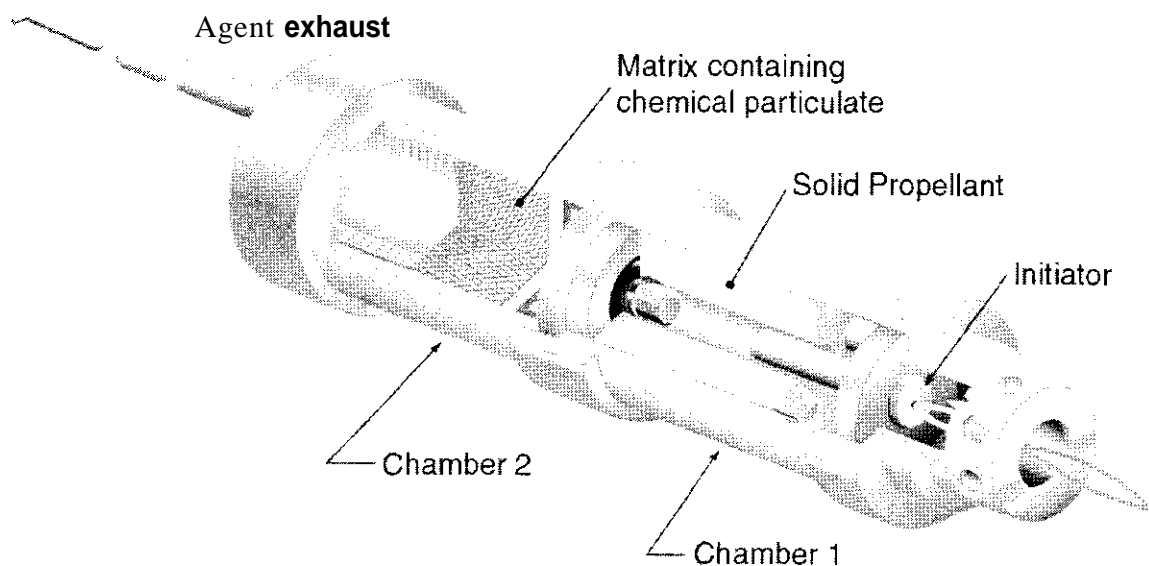
Figure 4. PAC Solid Propellant Gas Generator Test Unit.

determine the amount of initial agent required to put the JP-8 fire out. The relative efficiency of different agents was then ranked based upon their threshold quantity.

Various instrumentation was installed in the SPGG and test fixture to monitor and control test variables, and to make sure they are in the similar ranges from test to test. The SPGG was fired and the agent discharged after a steady-state fire was established. A waiting period of 45 sec between JP-8 fire on and SPGG firing was kept to assure steady-state, repeatable test conditions.

Some of the identified chemical agents, including KI, KBr, K_2CO_3, Fe_2O_3, Fe (oxalate), ferrocene and pentabromophenyl ether. were tested in a fire test fixture to evaluate their effectiveness in fire suppression for a controlled JP-8 fire. Table 4 summarizes the results of this testing. The agents were vaporized and delivered into the fire zone by high-temperature exhaust gases produced by a neutral-burning solid-propellant gas generator producing a blend of CO_2, N_2, and H_2O.

TABLE 4. SUMMARY OF NGP FTF DATA.

Neat Agent	Wt. (g)	Test No.	Result	Neat Agent	Wt. (g)	Test No.	Result
KI	20	027-06	Fire not out	Fe_2O_3	40	038-01	Fire not out
	40	027-07	Fire not out		80	038-02	Fire not out
	40	027-05	Fire out				
	60	027-04	Fire out				
KBr	40	032-02	Fire not out	Ferrocene	40	039-01	Fire not out
	60	032-03	Fire not out		80	039-02r	Fire not out
	60	032-01	Fire not out				
K_2CO_3	20	03.5-03	Fire not out	Iron Oxalate	40	040-01	Fire not out
	40	035-02r	Fire out	PBPE	60	041-01	Fire not out
	60	035-01	Fire out				

The test results indicated that K_2CO_3 and KI are more effective than KBr in suppressing JP-8 fire in the PAC Fire Test Fixture. The threshold amount for successful fire extinguishment seemed to be around 40 g of neat K_2CO_3 or KI powder used in each SPGG. As evidenced by some tests using agents with more distinctive colors, the powder seemed to be ejected out of the SPGG throughout the entire test duration of about 7.5 to 8 sec. Testing with ferrocene resulted in growth of needles of ferrocene crystals on the exit port of the delivery tube.

DISCUSSION

The cooler, high gas output propellant compositions described in Table 1 represent an important step towards increased efficiency SPGG fire suppression devices. Gas temperatures were reduced in some cases by 10–20% when compared to the current baseline. The findings of increased burn rate compositions, while maintaining relatively low gas temperatures, provide a means for further increases in agent cooling when these compositions are further modified with endothermic chemical coolants. Compositions incorporating combustion inhibitors were demonstrated to bum efficiently and were shown to be effective in fire suppression. It is interesting to note that the incorporation of species to suppress fires does not prevent combustion of the propellant.

Since the key to superagent effectiveness, e.g., iron pentacarbonyl, is the gas phase iron-oxo chemistry [8, 9], we considered developing alternative means to generating gas-phase or fine particulate iron oxide or other metallo-oxo species. This route then provides a means of delivering the chemical activity of $Fe(CO)_5$ without the associated toxicity. The routes explored to date, involving different means for potassium-oxo and iron-oxo containing discharges, have yielded ballistic characteristics that are amenable to further study.

With the test results available, it seemed that the iron-based agents and PBPE are less effective than KI and K_2CO_3, at least within the PAC Fire Test Fixture environment. The similarity in performance between the iodide and the carbonate is similar to that observed in turbulent spray burner testing at PAC; these data were interpreted as reflective of the greater role of the potassium ion in suppression effectiveness rather than the anion.

Assuming a uniform agent discharge, the agent to propellant weight ratio is about **4.3%** for threshold KI quantity. This is significantly lower than the **21 %** of KI in one of PAC's active propellants. Since the PAC KI-based active propellant has already been proven to be very effective in suppressing fires in some large-scale testing, the SPGG and propellant design could be further optimized to reduce weight and volume.

The lesser performance of the iron and pentabromo species seems to conflict with observations in some of the earlier literature. Several possible causes might contribute to this discrepancy. The residence time — and/or time at temperature for the given particle size of agent — may not be long enough for the agents to break down. Inadequate time at temperature is supported by the observation of ferrocene crystal growth at the end of the delivery tube, which implies sufficient stability of ferrocene in air at ~ 1000 °C for **0.3** s. Together, this indicates that the adequate agent delivery mechanism needs to be carefully designed and implemented in the solid-propellant fire extinguisher to utilize fully the chemical capabilities of such agents.

Although we have tried to keep all of the test variables as consistent as possible from test to test, the nature of this type of tests has shown certain degree of poor-repeatability in the test results. This non-repeatability is representative of the large-scale fire tests in which PAC has participated

in the past. It is also possible that the poor repeatability in some of the tests was due to the fact that the agent quantity used was in the threshold range. The threshold quantity may not be a sharp line separating the regions between fire out and fire not out. It might be a band accommo dating variations in test variables.

As a caution, ferrocene and its derivatives have been used in propellants as burn rate modifiers with great success; however. these compounds tend to migrate to the surface of the propellant where they are oxidized to ferrocinium compounds. Ferrocinium derivatives in combination with propellant ingredients give friction sensitive materials." This would tend to limit the use of I'erroccne derivatives to hybrid systems where the propellant and additive were stored separately.

SUMMARY

Several key findings have been made to date, whereby cooler propellant compositions have been used in conjunction with chemically active additives or combustion radical scavengers. Adding "radical traps" to the exhaust provides means for cooling, dilution. and chemical termination of the combustion process, hence increasing the overall effectiveness of the fire suppressant. Cur-rent propellant formulations arc lighter in weight than Halon 1301 for comparable fire suppres-sion effectiveness, but without the hazards associated with halon's ozone depletion capability.

The findings of this year's NGP effort suggest a more in-depth examination of the role and optimal delivery requirements for highly active, radical-scavenging chemical additives as fire suppressants. In addition to "pure" solid propellant approaches, the use of solid propellant/liquid (or gaseous) agent "hybrid" technologies shall also be explored.

Propellant development activities are planned in efforts to further optimize cool-burning, high-nitrogen content solid. Additionally, chemically active additives will be incorporated directly into propellant formulations and tested using the fire test fixture to *assess* effects of agent loading and combustion temperatures upon agent effectiveness.

Further optimization testing and of these compositions — in terms of agent temperatures, additive identity and loading—can he expected to result in substantial reductions in agent requirements. A system utilizing high-output, cool gas and chemical activity can be expected to result in agent loads of 1/3 – 1/5 that of the current baseline.

ACKNOWLEDGMENTS

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* R. Reed, personal communication. 1999.

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