U.S. ARMY RESEARCH, DEVELOPMENT AND ENGINEERING COMMAND

LOW GLOBAL WARMING POTENTIAL FIRE SUPPRESSANTS

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NO/LOW GWP FIRE SUPPRESSANTS

Background:

- The Kigali Amendment to the Montreal Protocol on Substances that Deplete the Ozone Layer will phase down production of hydrofluorocarbons (HFC) beginning in 2019.

- Joint TARDEC/AMCOM program to evaluate alternate materials for the high GWP extinguishing agents (HFC-227ea, HFC-125, etc.) currently deployed in ground and aviation weapon systems.

Objectives:

- Evaluation of the technical feasibility of emerging low GWP fire extinguishing agents for applicable weapons systems to guide future research and procurements:
  - Assessing the need for regulatory exemptions or reserve of high GWP agents if low GWP agents are not feasible
  - Meeting requirements that are unique to military applications (explosion suppression and vulnerability to ballistic threats)
  - Cost avoidance due to reduced availability, resulting in greater costs of high GWP agents after phase-down

Scope:

- Ground vehicle crew and engine compartments, aviation engine and auxiliary power unit (APU) compartments, and portable extinguishers.

KIGALI AMENDMENT TO MONTREAL PROTOCOL

- On 15 Oct 2016, Parties to the Montreal Protocol adopted the "Kigali Amendment" that adds HFCs to the Montreal Protocol and gradually reduces their consumption (production + imports - exports - destruction)

HFC Consumption Phase-Down Schedule

	Article 5 Group 1	Article 5 Group 2	Article 2
Baseline	2020-2022	2024-2026	2011-2013
Formula	Average HFC consumption	Average HFC consumption	Average HFC consumption
HCFC	65% of baseline	65% of baseline	15% of baseline*
Freeze	2024	2028	Not applicable
1st step	2029 – 10% Reduction	2032 – 10% Reduction	2019 – 10% Reduction
2nd step	2035 – 30%	2037 – 20%	2024 – 40%
3rd step	2040 – 50%	2042 – 30%	2029 – 70%
4th step	None	None	2034 – 80%
Plateau	2045 – 80%	2047 – 85%	2036 – 85%

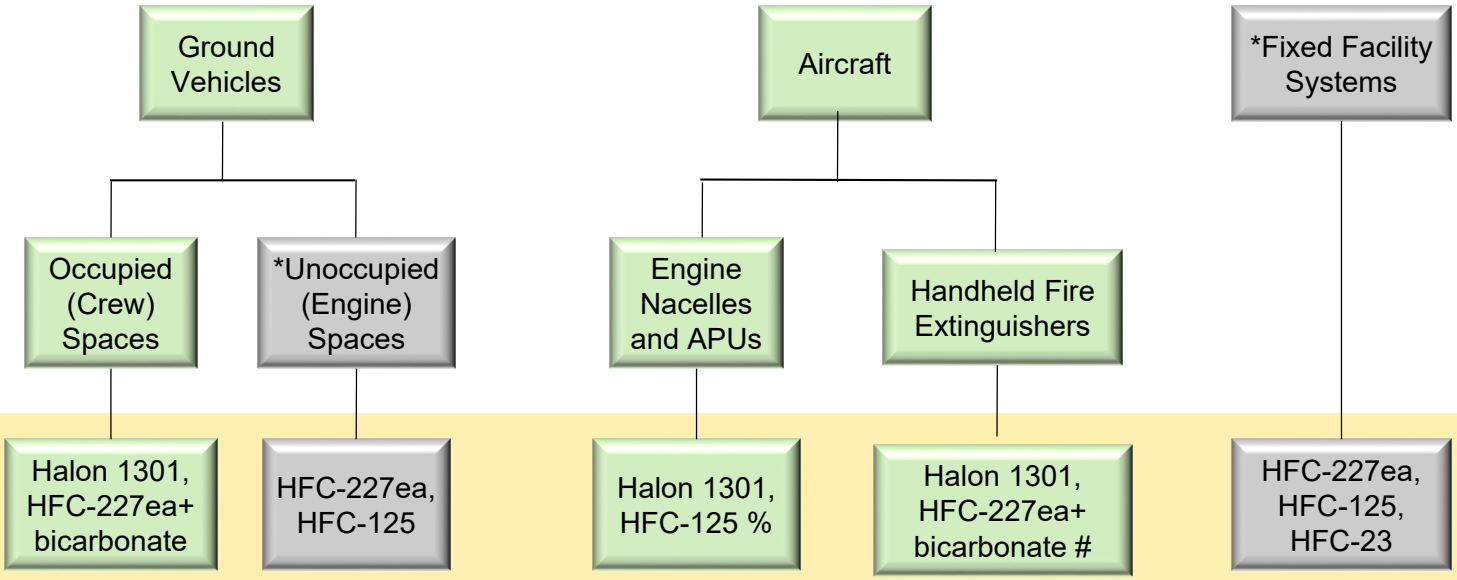
* For Belarus, Russian Federation, Kazakhstan, Tajikistan, Uzbekistan 25% HCFC component of baseline and different initial two steps (1) 5% reduction in 2020 and (2) 35% reduction in 2025

Group 1: Article 5 parties not part of Group 2

Group 2: GCC, India, Iran, Iraq, Pakistan

NO/LOW GWP FIRE SUPPRESSANTS

- Evaluating feasibility of low GWP chemicals to replace high GWP fire suppressants in Army weapon systems



* No projects planned
\# Army Aviation HFC-227ea/SBC HFEs under contract – fielding pending
% Army Aviation does not use HFC-125 in any system, however other DoD systems do

- Determine need for regulatory exemptions and/or strategic reserve of HFCs if low GWP chemicals do not prove feasible

CANDIDATE LOW GWP AGENTS

Material (1)	Potential Application			Key Findings
	HFE	Crew	Engine	
Solstice 1233zd	X		X	High byproduct levels
2-BTP	X		X	Low EC and LOAEL
Chemours TF-1/FC-1	X		X	High byproduct levels
Chemours SC-1 (3)	X		X	Moderate EC and byproducts
Opteon 1100 (HFO 1336mzz-Z) (3)	X		X	Moderate EC and byproducts
Opteon 1150 (HFO 1336mzz-E)	X	X	X	High EC and byproducts and LOAEL
Hexafluoropropene	X		X	High byproducts, Toxicology TBD
Chemours SC-2		TBD		Limited availability
E-Octafluoro-2-butene (2)		TBD		Toxicology TBD, Low BP, Limited availability
1,2,3,3,3-Pentafluorpropene		TBD		Toxicology TBD, Limited availability
2-Chloro-3,3,3-trifluorpropene		TBD		Toxicology TBD, Limited availability
Z-1,1,1,4,4,4-hexafluoro-2-butane		TBD		Toxicology TBD - possibly flammable
2,3,3,3-tetrafluorpropene		TBD		Toxicology TBD - possibly flammable
1-Chloro-1,3,3,3-tetrafluoropropene		TBD		Toxicology TBD - possibly flammable
AF11e				GWP and ODP unacceptably high
Solstice 1234ze				Flammability issue

(1) All agents except AF11e are alkenes which generally have short atmospheric lifetimes.

(2) Studied previously (NIST HOTWC report R0000270): cup-burner extinguishment 4.9%, bp 0.8 °C

(3) Chemours SC-1 and Opteon 1100 have been confirmed to be the same chemical per manufacturer

- Active evaluation
- Potential candidate
- Potential; higher risk
- Eliminated from consideration

CUP BURNER TESTING (NRL)

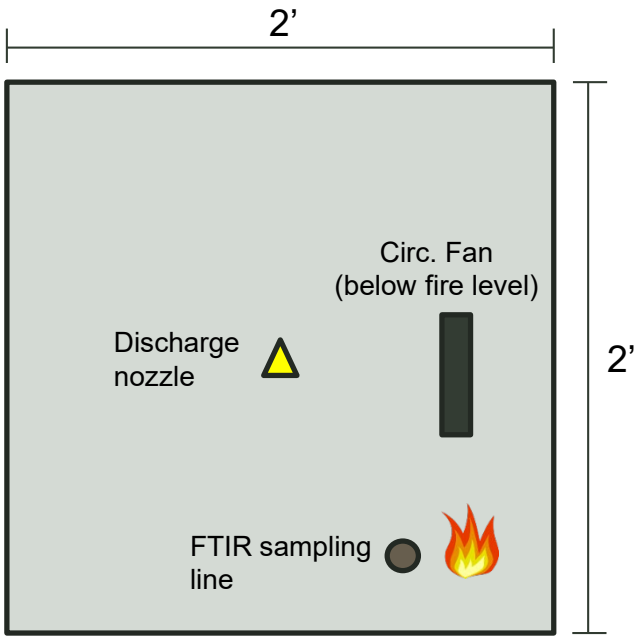
- The sub-scale (5/8) experimental setup able to accurately quantify flame extinction concentrations.
  - Test data with N_2 and halon 1301 compared to historical values (based on the full-scale cup burner) to ensure the setup gives consistent results.
- Validated experimental setup used to low GWP candidates on separate days to further verify consistency of results.
- Cup burner modified to improve agent introduction for some agents (i.e. 2-BTP)

Agent	Day 1 Avg EC	Day 2 Avg EC	Day 3 Avg EC	Total Avg EC
Solstice 1234ZE	6.31%	6.38%	6.51%	6.40%
Solstice 1233ZD	6.29%	5.73%	5.37%	5.80%
2-BTP	3.60%	4.92%	5.37%	4.63%
TF-1	5.21%	6.43%	5.43%	5.69%
Opteon 1150	3.99%	3.56%	3.40%	3.60%
Opteon 1100	7.57%	5.83%	6.61%	6.74%
Hexafluoropropene	5.64%	4.28%	5.58%	5.17%

SMALL-SCALE CHAMBER TESTING

	Extinguishing Concentration (cup burner)	Avg. Extinguishing Concentration	Byproduct Results (Peak)	
			HF	COF_2
2-BTP	4.6%	3.7%	20-50 ppm	20-60 ppm
Solstice 1233zd	5.8%	7-10%	1800 ppm	560 ppm
Chemours TF-1	5.7%	7.7%	1280 ppm	260 ppm
Hexafluoropropene	5.2%	10.5%	2800 ppm	585 ppm
Opteon 1150	3.6%	11.3%	1350 ppm	315 ppm
Opteon 1100	6.7%	9.1%	310 ppm	80 ppm
Halon 1301	2.9%	3.0%	BDL	BDL
FM200	6.7%	8.9-11.0%	BDL	BDL
FM200+SBC	6.7%	5.0-6.5%	BDL	BDL

BDL – below detection limit (~20 ppm)



Overhead view of 8 ft^3 chamber

Halon 1301 and FM-200 used as baselines to verify chamber performance

2-BTP shows potential as a total flooding and streaming compound

1233zd shows potential as a streaming compound

TF-1 shows potential as a total flooding compound. Only available in experimental quantities

1234ze reacted violently and generated high levels of acid gases; will not be pursued further

Opteon 1150 has a low cup burner value but higher concentration required in the chamber testing

Hexafluoropropene produced high byproduct concentrations relative to other materials

TOXICOLOGY

- The safe level for HFCs and most alternate agents is intended to prevent cardiac sensitization, a condition in which the heart may become sensitized to catecholamines (i.e., adrenaline) increasing the risk of cardiac arrhythmia.
  - Criteria are based on animal studies and pharmacokinetic modeling.
  - Criteria are available for the primary agents under consideration.
- Most of the fluoroalkene agents considered have little to no toxicology data available for either acute inhalation toxicity or cardiac sensitization.
  - Animal studies would be required to fill toxicity data gaps and derive safety criteria if these candidates meet other performance requirements.
- In the case of hexafluoropropene, acute inhalation toxicity from kidney effects may be a greater limiting factor than cardiac sensitization.
- Combustion byproducts of primary concern are hydrogen fluoride (HF) and carbonyl fluoride (COF_2).
  - COF_2 toxicity is recognized to be higher than HF and a greater limiting factor.
  - Based on experience with FM200-BC, the use of blends with dry powder is considered critical for reducing byproducts of the alternative agents.

	HFC-227ea (FM-200)	2-BTP	Solstice PF (Solstice 1233 zd)	Opteon 1100 (HFO-1336mzz-Z)	Opteon 1150 (HFO-1336mzz-E)
CAS	431-89-0	1514-82-5	102687-65-0	692-49-9	66711-86-2
IUPAC name and structure	1,1,1,2,3,3,3-Heptafluoropropane	2-Bromo-3,3,3-trifluoro-1-propene	Trans-1-chloro-3,3,3-trifluoropropene	(Z)-1,1,1,4,4,4-Hexafluoro-2-butene	(E)-1,1,1,4,4,4-Hexafluoro-2-butene
	(CF3-CHF-CF3)	(CF3CBr=CH2)	(CF3CH=CHCl)	(CF3CH=CHCF3)	(CF3CH=CHCF3)
LOAEL (%)	10.5	1 (Madden, 2014)	2.5	2.5	7.0
NOAEL (%)	9.0	0.49 (Huntington, 2002)	2.5	1.25	7.0
8-hr TWA (ppm)	1,000	11.0 (proposed)	800	500	?

Handheld Extinguisher Testing

PERFORMANCE SUMMARY (97 IN^3 CYLINDER)

Agent	SBC Type	SBC Percent	Largest Successful Extinguishment
2-BTP	-	-	5B (12.5 ft^2)
Honeywell Solstice ZD	-	-	2B (5 ft^2)
Honeywell Solstice ZD	SBCs	5	3B (7.5 ft^2)
Honeywell Solstice ZD	KSA	10	3B (7.5 ft^2)
Chemours Opteon 1100	-	-	2B (5 ft^2)
Chemours Opteon 1150	-	-	3B (7.5 ft^2)
Chemours Opteon 1150	KSA	5	3B (7.5 ft^2)

DISCUSSION ON PERFORMANCE

- 2-BTP did not seem to blend as easily with SBCs and KSA as some of the other agents. Limited blended testing was conducted but additional studies would be useful to determine the interaction between 2-BTP and SBCs.

- Honeywell Solstice ZD and Chemours Opteon 1150 performed adequately as blended agents – further optimization to increase flow and improve discharge pattern is desired to see if performance can be increased.

- Opteon 1150 has a lower boiling point than many no/low GWP compounds which can be beneficial in fire extinguishing applications.

- Testing with Opteon 1100 as a blended agent was not conducted due to limited time and material.

ENGINE NACELLE 2-BTP TESTING

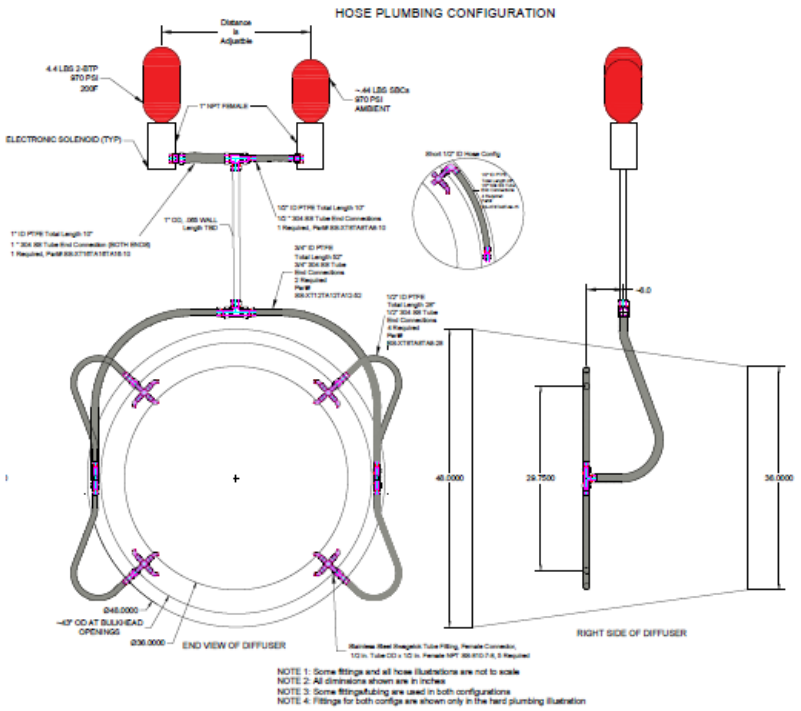
- Previous testing with 2-BTP (2004) did not demonstrate acceptable performance.
  - high and **low airflow**
  - **fuel spray** and pan fires

- 2-BTP's higher boiling point (93°F) slows rate of vaporization and time to reach design concentration.

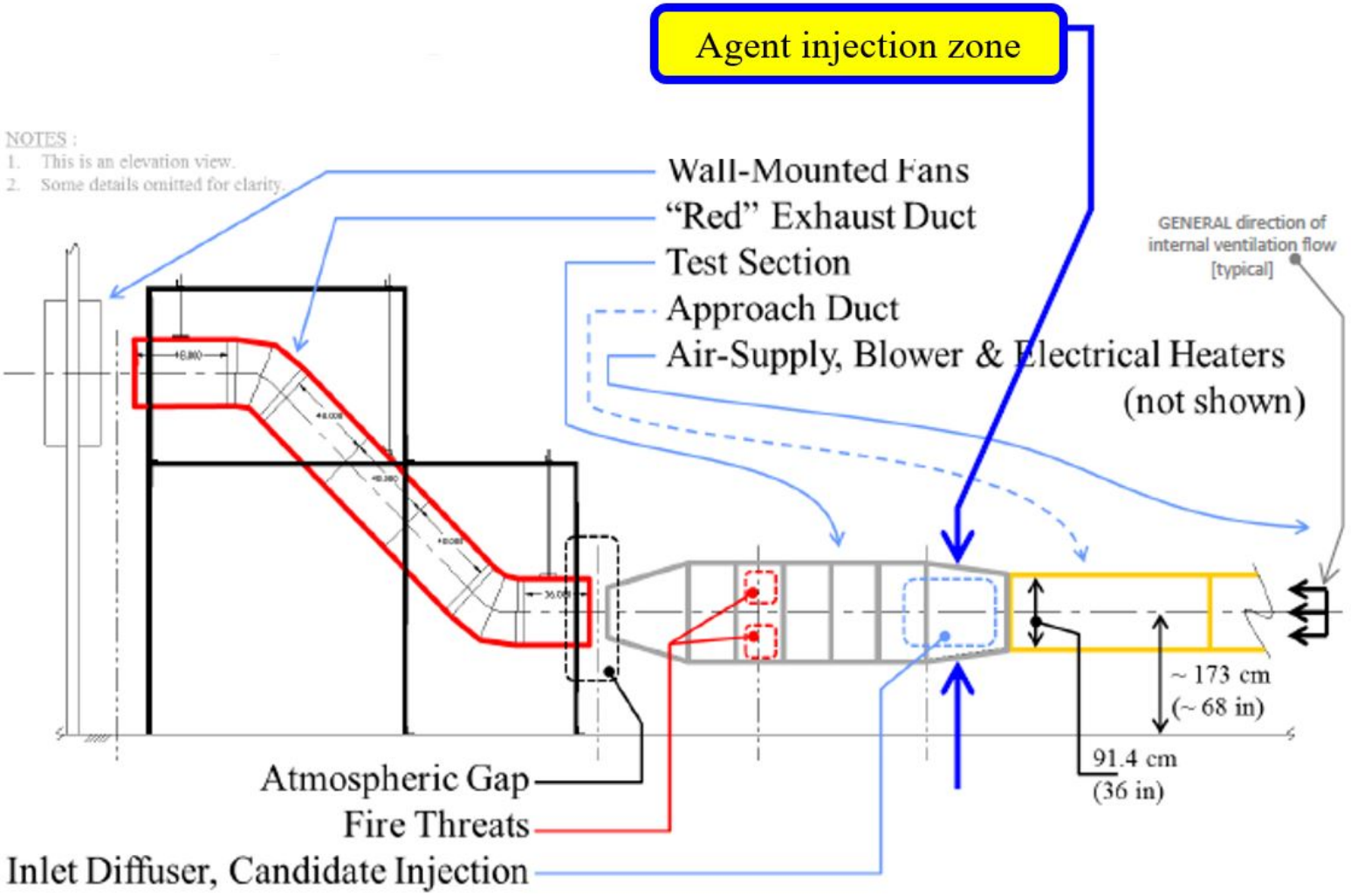
- Testing evaluated ambient and heated 2-BTP (185°F simulating a SPGG configuration) to speed up vaporization and added micronized SBC
  - extinguishment
  - post extinguishment overpressure
  - Time to reflash

- Configuration similar to 2004 testing
  - distribution through an array of 12 nozzles
  - 4.4 lbs. of 2-BTP at 970 psi
  - 0,44 lbs. of SBC also added

- 6-17 Aug testing at FAA Tech Center leveraged work conducted by industry



Engine Nacelle Testing



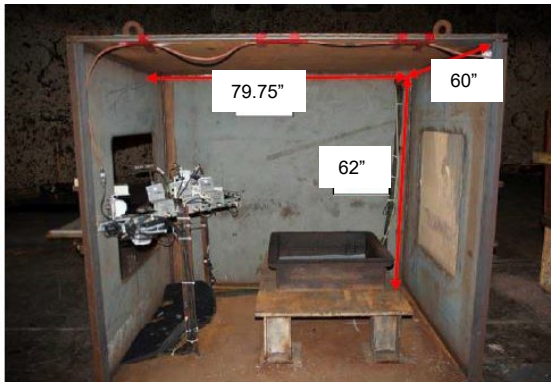
Schematic of FAA TC test facility

ENGINE NACELLE FIRE TESTING

- Previous testing with 2-BTP ended with negative results due to fuel reignition within the test fixture. FAATC described the phenomena as an audible cue or thud, with one particular instance louder than the rest.
- Attempts to reduce or eliminate the negative results were two-fold:
  - Heat the 2-BTP prior to discharge to simulate a solid propellant gas generator (SPGG). Each cylinder was heat soaked to 185°F.
  - A 10% by weight charge of specialized sodium bicarbonate (SBCs) was also injected with the 2-BTP. SBCs have been shown to assist in fire suppression and decomposition product reduction.
  - Each test used 4.4 lb. of 2-BTP w or w/o 0.44 lb. of SBCs
- General trend showed a possibility of improvement over ambient 2-BTP testing conducted previously

  SPGG and SBCs blend optimization with 2-BTP and other low BP/low GWP candidates would be worth exploring further

FUEL-SPRAY FIRE TESTING



- Candidates are being tested in a 172 ft^3 crew compartment mockup in both open and cluttered configurations.
- Agent down-select and design concentrations based on small-scale test results.
- Testing to verify laboratory results and determine agents for further development in full-up vehicle.
- Testing started 17 Sep

Parameter	Requirement
Fire Suppression	Extinguish all flames without reflash
Skin Burns	Less than second degree burns (<2400°F-sec over 10 seconds or heat flux < 3.9 cal/cm^2)
Overpressure	Less than 11.6 psi lung damage/ 4 psi eardrum rupture
Agent Concentration	Not to exceed Lowest Observed Adverse Effects Level
Acid Gases ($HF + HBr + 2 \cdot COF_2$)	Less than 746 ppm-min (5 min dose)
Oxygen Levels	Not below 16%-

Agent	Starting Quantity
Calibration	N/A
Baseline (FM200BC)	10lbs + 10% BC
BC Dry Chemical, regular	3.75 lbs
BC Dry Chemical, nano	3.75 lbs
BC Dry Chemical, mix	TBD
HFO-1233zd(BC)	7lbs + 10% BC
Opteon 1100(BC)	8lbs + 10% BC
Opteon 1150(BC)	6.5lbs +10% BC
2-BTP	6.5lbs + 10% BC

Starting quantity: minimum design concentration

Summary/Conclusions

- Results to date indicate that most currently available candidate low GWP agents:
  - Have shown varying levels of firefighting performance
  - Exhibit more reactivity than current HFCs resulting in elevated byproduct levels
  - May require greater reliance on powder additives than current HFCs to achieve required performance
  - May have performance further improved by additional delivery system development

Ongoing Activities

- Complete abbreviated handheld extinguisher development
- Complete full-scale crew AFES testing with multiple candidates
- Analyze engine nacelle testing results from FAA Tech Center
- Prepare summary report documenting findings
- Continue to pursue additional funding sources to advance this effort