LABORATORY-SCALE STREAMING TESTS OF ADVANCED AGENTS

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INTRODUCTION

Mainstream Engineering Corporation has been performing research on halon replacements for several years [1-7]. Our approach to the problem has been to apply the complex yet accurate techniques of computational chemistry to screen previously untested compounds as halon replacements. Computational chemistry techniques allowed for accurate prediction of the key fire suppression properties of a large list of compounds not previously considered as halon replacements. Compounds with a high probability for success were then evaluated in the laboratory to test the computational chemistry predictions.

This approach was used successfully to develop three advanced replacement agents with performance comparable to the existing halons without the atmospheric reactivity. These compounds were found to be highly efficient, nontoxic, and environmentally friendly. Table 1 lists the key properties of these promising halon replacements. Table 1 shows that the three candidate replacements are extremely promising. Other property measurements performed on the candidate replacement agents included vapor pressure measurements and materials compatibility experiments. The candidate agents were found to be compatible with common metal and elastomer samples tested. The candidate halon replacements listed in Table **1** are currently being patented as fire suppression agents by Mainstream Engineering Corporation.

To continue further development of these halon replacements for military and commercial use, laboratory-scale streaming experiments were performed. The test results for the agent candidates were compared to the performance of baseline streaming agents. Table 2 lists the candidate and baseline agents evaluated, along with their suppliers.

Table 1. Key Properties of Candidate Halon Replacements.

Agent	Octafluoro-2-butene	Perfluoro-2-butyltetrahydrofuran	Heptafluoropropyl-1,2,2,2-tetrafluroethyl Ether
Cup-burner FEC	4.9	3.5	**4.3**
ODP	Zero	Zero	Zero
15 minute LC_{50}	> 9%"	Nontoxic[b]	Nontoxic[b]
Residue Level	Zero	Zero	Zero
Cardiac Sensitization NOAEL (v/v%)	13.8%[c]	6.5%[c]	21.6%'
Tropospheric Lifetime (years)[c]	0.5	2.85	2.7
Boiling Point ("C)	0.8	104.8	42.8
Application	Flooding or Streaming	Streaming	Streaming

"No mortalities at 90,000 ppm for 15 min (+ 23 min chamber equilibration).

[b] Has been used as a blood substitute.

[c] Calculated by quantitative structure-property relationship (QSPR).

Table 2. Agents Tested.

Agent Name	Supplier	Use
octafluoro-2-butene	SynQuest Laboratones, Inc.	candidate
heptafluoropropyl-1,2,2,2-tetrafluoroethyl ether	SynQuest Laboratories, Inc.	candidate
perfluoro-2-butyltetrahydrofuran	PCR, Inc.	candidate
perfluorohexane	3M	standard
trifluoroiodomethane	Deep Water Inc.	standard
bromochlorodifluoromethane (Halon 1211)	Feecon, Corp.	standard
1,1,1,3,3,3-hexafluoropropane (HFC-236fa)	DuPont	standard
1-bromopropane[a]	Aldrich Chemical Co.	candidate

[a] 1-bromopropane was blended with octafluoro-2-butene and with HFC-236fa.

STREAMING TEST APPARATUS

The laboratory-scale streaming test apparatus at WL/FIVCF, Tyndall AFB, Florida was used for all streaming tests. This apparatus consists of a 300-ml stainless steel sample cylinder, an electronic balance, a support stand, a manually-activated solenoid valve, an agent discharge nozzle and fittings, a square fire pan (20 cm x 20 cm x 2.5 cm), and 1/8-in OD Teflon connecting tubing. The sample cylinder was supported on top of an Ohaus Model TS4KS electronic balance

(M.l g) to allow measurement of agent discharge. Argon overpressures ranging from 60 psig to 150 psig were applied to the sample cylinder. The nozzle is gimbal mounted for simultaneous vertical/horizontal motion. The vertical motion on the nozzle allowed for moving the spray of agent from the front to the back of the fire pan. The horizontal motion of the pivot allowed for covering the entire width of the fire pan. The horizontal distance from the nozzle tip to the fire pan was 180 mm. The nozzle was typically set at a vertical height of 330 mm (this height was adjustable). This provided a 61.4 deg angle of attack from the vertical.

All nozzles used in the testing were Unijet'' spray nozzles manufactured by Spraying Systems, Co. (Wheaton, E). Nozzles with full cone or flat spray patterns were used. Table 3 provides performance data on the nozzles used.

Table **3.** Performance Data for Unijet'' Nozzles

Nozzle	Orifice Diameter (in.)	Nozzle	Orifice Diameter (in.)
0.7 Cone	0.030	150067 Flat	0.021
0.5 Cone	0.024	150050 Flat	0.018
0.4 Cone	0.022	250050 Flat	0.018
0.3 Cone	0.020	150033 Flat	0.015
1501 Flat	0.026	150025 Flat	0.013

STREAMING TEST PROCEDURE

1. Fill the sample cylinder with sufficient amount of agent and apply argon overpressure.
2. Fill the fire pan with 500 ml. of n-heptane fuel.
3. Ignite the fuel, and allow for 10-sec fuel preburn.
4. Apply the agent to the fire pan. The agent was typically applied to the front of the pan first, and drove to the back of the pan.
5. Continue fighting the **fire** until the fire is extinguished.

TEST RESULTS AND DISCUSSION

Streaming tests were performed at the WL/FIVCF Fire Research Laboratory from 28-30 April 1997 and from 21-25 July 1997. All tests were recorded on videocassette. The primary goal of the tests was to obtain a comparison of the effectiveness of the candidate agents with the agent standards. The experiments were aimed at determining the minimum application density of agent that would extinguish the fire. For each experiment, the various experimental variables, such as agent type, nozzle type, argon overpressure, preburn time, and fuel volume were noted.

For each combination of agent, nozzle, and overpressure, agent mass flow rates were measured. Three measurements were made for each agent/nozzle/pressure combination and averaged. Application densities, defined as the mass flow rate divided by the surface area of the fire, were calculated from the averaged flow rate. It was felt that the application density would be a parameter that would scale from lab scale fires to larger fires.

The primary experimental result was whether or not the fire was extinguished. The secondary experimental result was the extinguishment time, which was determined from viewing the videotape. Because of permissible operator technique in fighting the fire, extinguishment times were found to have variability and were considered a secondary experimental result. Extinguishment times of less than approximately 10 sec indicated that the agent readily extinguished the fire. Extinguishment times in excess of approximately 10 sec indicated that the agent was near its minimum application density. From the agent application density and extinguishment time, the mass of agent required to extinguish the fire could also be calculated.

Perfluorohexane Results

Application densities of 2.95 lbs/ft^2-min and 3.25 lbs/ft^2-min were evaluated with the flat spray nozzle. An application density of 2.95 lbs/ ft^2-min did not extinguish the fire. Four successful extinguishments resulted with an application density of 3.25 lbs/ft^2-min. Three successful extinguishments resulted using the full cone spray nozzle with an application density of 3.05 lbs/ft^2-min. Table 4 summarizes the test results for perfluorohexane.

Table 4. Test Results for Perfluorohexane.

Nozzle	Pres. (psig)	Application Density (lbs/ft^2-min)	Average Exting. Time (sec)	Average Agent Mass (g)
1501 Flat	85	2.95	No Ext.	No Ext.
1501 Flat	100	3.25	10.3	95.8
0.5 Cone	100	3.05	6.3	55.6

The minimum application density for perfluorohexane with the flat spray nozzle is in the range of 3.0 *to* 3.3 lbs/ft^2-min. The full cone nozzle was only slightly more. effective than the flat spray nozzle for perfluorohexane, requiring slightly less agent mass and less time to extinguish the fire at a slightly lower application density. The minimum application density for perfluorohexane with the full cone nozzle is estimated to be in the range of 2.8-3.1 lbs/ft^2-min.

Perfluoro-2-butyltetrahydrofuran Test Results

Perfluoro-2-butyltetrahydrofuran was evaluated with both the flat spray and the full cone nozzles. This agent candidate did not extinguish the fire, in fact, it actually appeared to fuel the fire, resulting in a larger fire with significant smoke and soot formation. Even using *the* 0.7 cone nozzle, with a higher mass flow rate than the 0.5 cone nozzle, no extinguishment of the fire resulted. Further testing with this agent was stopped, and no flow rates or application densities were measured for this agent. Table 5 shows the testing results of this agent.

Table 5. Test Results for Perfluoro-2-butyltetrahydrofuran.

Nozzle	Pres. (psig)	Application Density (lbs/ft^2-min)	Average Exting. Time (sec)	Average Agent Mass (g)
1501 Flat	100	No Data	No Ext.	No Ext.
0.5 Cone	100	No Data	No Ext.	No Ext.
0.7 Cone	100	No Data	No Ext.	No Ext.

Heptafluoropropyl-1,2,2,2-tetrafluoroethyl Ether Test Results

Application densities of 3.05 lbs/ft^2-min and 3.77 lbs/ft^2-min were evaluated with the flat spray nozzle. Three successful extinguishments resulted at both of those application densities. Tests with the full cone spray nozzle evaluated application densities of 3.11 and 3.91 lbs/ft^2-min. No extinguishment was achieved with this nozzle type. Table 6 summarizes the test results for this agent. Based on these data, the minimum application density for heptafluoropropyl-1,2,2,2-tetrafluoroethyl ether using the flat spray nozzle **is** approximately 3.05 lbs/ft^2-min. The minimum application density with the full cone nozzle is considerably higher, greater than 3.91 lbs/ft^2-min.

Table 6. Test Results for Heptafluoropropyl-1,2,2,2-tetrafluoroethyl Ether.

Nozzle	Pres. (psig)	Application Density (lbs/ft^2-min)	Average Exting. Time (sec)	Average Agent Mass (g)
1501 Flat	100	3.05	25.5	224
1501 Flat	150	3.71	3.3	36.1
0.5 Cone	150	3.91	No Ext.	No Ext.

Octafluoro-2-butene Test Results

Application densities of 2.28, 2.58, and 3.23 lbs/ft^2-min were evaluated with the flat spray nozzles. An application density of 2.28 lbs/ft^2-min only extinguished the fire one out of three attempts. Application densities of 2.58 and 3.23 lbs/ft^2-min successfully extinguished the fire each of three times. Based on these data, the minimum application density for octafluoro-2-butene using the flat spray nozzle is in the range of 2.28-2.58 lbs/ft^2-min.

Application densities of 2.51 and 3.12 lbs/ft^2-min were evaluated with the full cone spray nozzles. An application density of 2.51 lbs/ft^2-min failed to extinguish the fire. An application density of 3.12 lbs/ft^2-min successfully extinguished the fire each of three times. The minimum application density for octafluoro-2-butene using the full cone spray nozzle is in the range of 2.51 to 3.12 lbs/ft^2-min. Table 7 summarizes the test results for this agent.

Table 7. Test Results for Octafluoro-2-butene.

Nozzle	Pres. (psig)	Application Density (lbs/ft^2-min)	Average Exting. Time (sec)	Average Agent Mass (g)
1501 Flat	100	3.23	8.9	55.1
150067 Flat	100	2.58	17.6	130
150050 Flat	100	2.28	9.7 [a]	63.8 [a]
0.5 Cone	100	3.12	8.3	74.9
0.4 Cone	100	2.51	No Ext.	No Ext.

[a] Extinguishment only achieved one of three attempts.

Halon 1211 Test Results

Halon 1211 was evaluated with application densities of 2.40, 2.11, 1.76, and 1.36 lbs/ft^2-min with the flat spray nozzle. Application densities of 2.40, 2.11, and 1.76 successfully extinguished the fire each time tested. An application density of 1.36 lbs/ft^2-min extinguished the fire only one in three times. These data suggest that the minimum application density for Halon 1211 with the flat spray nozzle is approximately 1.36 lbs/ft^2-min. An application density of 1.49 lbs/ft^2-min was also evaluated with the full cone nozzle, successfully extinguishing the fire. More data are required to determine the minimum application density for Halon 1211 using the full cone nozzle. Table 8 presents the Halon 1211 results.

Table 8. Test Results for Halon 1211.

Nozzle	Pres. **(psig)**	Application Density (lbs/ft^2-min)	Average Exting. Time (sec)	Average Agent Mass (g)
150050 Flat	100	2.40	2.2	14.9
150033 Flat	100	2.11	1.2	7.1
150025 Flat	100	1.76	7.7	37.6
150025 Flat	60	1.36	6.9 [a]	26.3[a]
0.3 Cone	100	1.49	5.1	21.9

[a] Extinguishment only achieved one of three attempts.

Trifluoroiodomethane Test Results

Trifluoroiodomethane was evaluated with only the full cone nozzles. ***An*** application density of 0.89 lbs/ft^2-min required an average of 7.8 grams of agent to extinguish the fire with an average extinguishment time of 3.0 sec. A higher application density was also evaluated that extinguished the fire in less than 1.0 sec, overpowering the fire. Table 9 summarizes the data obtained for this agent. The data for this agent were insufficient to determine the minimum application density, however, it is less than 0.89 lbs/ft^2-min.

Table 9. Test Results for Trifluoroiodomethane.

Nozzle	Pres. (psig)	Application Density (lbs/ft^2-min)	Average Exting. Time (sec)	Average Agent Mass (g)
0.5 Cone	100	Not Measured	0.8	Not Measured
0.3 Cone	100	Not Measured	1.2	Not Measured
0.3 Cone	60	0.89	4.0	10.2

HFC-236fa Results

HFC-236fa was evaluated with the flat spray nozzles at application densities of 3.52, 2.48, 2.38, 1.80, 1.65, and 1.49 lbs/ft^2-min. Application densities of 3.52, 2.48, and 2.38 lbs/ft^2-min successfully extinguished the fire for all tests. Application densities of 1.80 and 1.65 lbs/ft^2-min extinguished the fire two out of three tests each. An application density of 1.49 lbs/ft^2-min did not extinguish the fire. Based on this data, the minimum application density for HFC-236fa using the flat spray nozzle is in the range of 1.65-1.80 lbs/ft^2-min. Table 10 summarizes the test results for this agent.

Table 10. Test Results for HFC-236fa.

Nozzle	Pres. (psig)	Application Density (lbs/ft^2-min)	Average Exting. Time (sec)	Average Agent Mass (g)
1501 Flat	100	3.52	2.2	21.7
150067 Flat	100	2.48	5.0	34.4
150050 Flat	100	2.38	6.0	39.8
150033 Flat	100	1.80	5.2"	26.1"
150033 Flat	80	1.65	6.7"	30.6"
150025 Flat	100	1.49	No Ext.	No Ext.

[a] Extinguishment only achieved two of three attempts.

Octafluoro-2-butene and 1-Bromopropane Blends

Various concentrations of 1-bromopropane were blended with octafluoro-2-butene and evaluated with the flat spray nozzle. Concentrations of 1-bromopropane in octafluoro-2-butene of 5.5, 7.0, 8.0, and 15 wt.% were evaluated. Table 11 summarizes these test results. The addition of 1 bromopropane resulted in reduced agent amounts and extinguishment times compared to octafluoro-2-butene alone. The data of Table 10 suggest that the optimum blend is 7 wt.% 1 bromopropane, with a minimum application density of 1.47 lbs/ft^2-min. This compares to octafluoro-2-butene alone, which had a minimum application density of 2.28-2.58 lbs/ft^2-min under similar conditions.

HFC-236fa and 1-Bromopropane Blends

A 5 wt.% blend of 1-bromopropane with HFC-236fa was evaluated with the flat spray nozzle. Table 11 summarizes these test results. The addition of 1-bromopropane only slightly reduced the agent amounts and extinguishment times compared to HFC-236fa alone. The data (Table 12) suggest that the minimum application density is approximately 1.55 lbs/ft^2-min for this blend. This compares to HFC-236fa alone, which had a minimum application density of 1.65-1.80 lbs/ft^2-min. under similar conditions.

Table 11. Test Results for Octafluoro-2-butene/1-Bromopropane Blend.

Wt.% 1-bromopropane	Nozzle	Pres. (psig)	Application Density (lb/ft^2-min)	Avg. Exting. Time (sec.)	Average Agent Mass (g)
15.0	150050 Flat	100	2.35	4.6	30.3
15.0	150033 Flat	100	1.82	No Ext.	No Ext.
8.0	150033 Flat	100	1.90	11.5	61.0
8.0	150025 Flat	100	1.57	7.3	32.1
8.0	150025 Flat	60	1.47	40.2	165.1
7.0	150033 Flat	100	1.82	7.4"	37.5[a]
5.5	150050 Flat	100	2.55	3.6	25.5
5.5	150033 Flat	100	2.01	No Ext.	No Ext.

[a] Extinguishment only achieved two of four attempts.

Table 12. Test Results for HFC-236fa/1-Bromopropane Blend.[a]

Wt.% 1-bromopropane	Nozzle	Pres. (psig)	Application Density (lb/ft^2-min)	Avg. Exting. Time (sec.)	Average Agent Mass (g)
5.0	150033 Flat	80	1.55	7.0	30.4

[a] Extinguishment only achieved two of four attempts.

Comparison of Agents

The data contained in Tables 4-12, along with the minimum application densities, can be used to compare the various agents tested. For agents with differing minimum application densities for the different nozzle spray patterns, the nozzle with the lowest minimum application density was selected. Table 13 compares the agents based on minimum application densities.

The experimental data show that trifluoroiodomethane and Halon 1211 were the most effective agents tested, with minimum application densities of < 0.89 and 1.36 lbs/ft^2-min, respectively. The octafluoro-2-butene/1-bromopropane blend (92:8) was the next most effective agent with a minimum application density of 1.47 lbs/ft^2-min. The HFC-236fa/1-bromopropane blend was the next most effective with a minimum application density of 1.55 lbs/ft^2-min. HFC-236fa and octafluoro-2-butene alone had minimum application densities in the range of 1.65 - 1.80 and 2.28 - 2.58 lbs/ft^2-min, respectively. Perfluorohexane and heptafluoropropyl-1,2,2,2-tetrafluoroethyl ether performed similarly, with minimum application densities ranging from about 2.8-3.1 lb/ft^2-min. **Peffluoro-2-butyltetrahydrofuran was** ineffective at extinguishment.

Table 13. Streaming Agent Comparison.

Agent	Minimum Application Density (lbs/ft^2-min)	Nozzle Type
trifluoroiodomethane	< 0.89	Full Cone
Halon 1211	1.36	Flat Spray
octafluoro-2-butene/1-bromopropane (92:8)	1.41	Flat Spray
HFC-236fa/1-bromopropane (95:5)	1.55	Flat Spray
HFC-236fa	1.65 - 1.80	Flat Spray
octafluoro-2-butene	2.28 - 2.58	Flat Spray
perfluorohexane	2.8 - 3.1	Full Cone
heptafluoropropyl-1,2,2,2-tetrafluoroethyl ether	3.11	Flat Spray
perfluoro-2-butyltetrahydrofuran	No Extinguishment	Either

The streaming performances of the two blends evaluated were very close to that of Halon 1211. The minimum application density of the octafluoro-2-butene/1-bromopropane blend (92:8) was only 8.1% higher than that of Halon 1211. The minimum application density of the HFC-236fa/1-bromopropane blend (95:5) was 14.0% higher than that of Halon 1211. Octafluoro-2-butene has properties that compare favorably to HFC-236fa, as shown in Table 14. Also, Table 1 shows that inhalation toxicity data on this compound **are** favorable.

Table 14. Atmospheric Properties of Octafluoro-2-butene and HFC-236fa.

Property	Octafluoro-2-butene	HFC-236fa
Tropospheric Lifetime (yrs.)	1.14 yrs. (QSPR)	95.6 yr. (literature)
GWP	972 (QSPR)	6300 (literature)
Cardiac NOAEL	13.7% (QSPR)	10.0% (literature)

FUTURE WORK

The follow-on effort to this work has begun, which will involve further development of octafluoro-2-butene and blends of octafluoro-2-butene with tropodegradable bromocarbons. The follow-on effort will have the following objectives:

1. Perform large-scale tests fire suppression tests (both streaming and flooding) with octafluoro-2-butene and mixtures of octafluoro-2-butene with tropodegradable bromocarbons.
2. Determine cardiac sensitization no observed adverse effect levels (NOAEL) with octafluoro-2-butene and mixtures of octafluoro-2-butene with tropodegradable bromocarbons.
3. Perform inhalation toxicity testing with octafluoro-2-butene and mixtures of octafluoro-2-butene with tropodegradable halocarbons. This testing would be aimed at determining LC_{50} concentrations.

4. Atmospheric lifetime and GWP studies should be performed with octafluoro-2-butene and mixtures of octafluoro-2-butene with tropodegradable halocarbons. This could involve measuring the reaction rate constants of these agents with hydroxyl radicals, as well as measuring the infrared absorption characteristics of the agents.
5. The ODPs of any tropodegradable halocarbons blended with octafluoro-2-butene should be determined. Octafluoro-2-butene has an ODP of zero.
6. Determine the key physical and thermodynamic properties of the agents.
7. Flow discharge analysis should be performed with the agents to allow for optimal design of complete fire suppression systems.
8. Identification of manufacturing procedures to minimize the cost of production of the agents should be developed.
9. Other testing and/or measurements required for EPA SNAP approval should be determined, and application for EPA SNAP approval should be completed.

CONCLUSIONS

The streaming tests showed that trifluoroiodomethane and Halon 1211 were the most effective agents tested. The blends of octafluoro-2-butene with 1-bromopropane and HFC-236fa with 1-bromopropane had performance similar to Halon 1211, with minimum application densities only 8.1% and 14.0% higher than Halon 1211, respectively. The pure agents HFC-236fa and octafluoro-2-butene followed, with higher minimum application densities than when blended with 1-bromopropane. Perfluorohexane and heptafluoropropyl-1,2,2,2-tetrafluoroethyl ether appear perform similarly, but significantly higher than Halon 1211. Perfluoro-2-butyltetrahydrofuran was ineffective at extinguishment.

The octafluoro-2-butene blends with 1-bromopropane (or other tropodegradable bromocarbons) are attractive replacements for Halon 1211. Octafluoro-2-butene has atmospheric properties that compare favorably to HFC-236fa, with a significantly lower atmospheric lifetime and GWP. QSPR predictions of cardiac sensitization NOAEL also suggest favorable characteristics. Inhalation toxicity tests performed at 9% for **15** min also showed no toxic effect.

Further work with octafluoro-2-butene and mixtures of octafluoro-2-butene with tropodegradable bromocarbons is underway. This work would include performing large-scale fire suppression tests, determining cardiac sensitization NOAEL, determining LC_{50}, performing atmospheric impact studies (lifetime, GWP, ODP), performing flow discharge analysis, reducing manufacturing costs, and applying for EPA SNAP approval.

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