

# TESTING RESULTS OF STREAMING AGENT REPLACEMENTS FOR HALON 1211

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## INTRODUCTION

This paper is focused on the testing of octafluoro-2-butene and blends of octafluoro-2-butene with 1-bromopropane for streaming fire suppression applications. The project involved performing large-scale fire suppression tests, determining the toxicity characteristics of the agents, determining the cardiac sensitization NOEL of the candidate agents, determining the atmospheric impact of the agents, performing materials compatibility experiments, determining the agent decomposition products, characterizing the physical properties of the agents, and assessing the manufacturability of the agents. Reference 1 is the complete report on the project.

## LARGE-SCALE FIRE SUPPRESSION TESTING

Large-scale fire suppression testing was performed at the intermediate-scale 3D test fixture at Tyndall AFB. AFRL firefighters performed the tests. The test plan called for testing a 25 ft<sup>2</sup> JP-8 pan fire. Halon 1211 was the baseline agent, and the candidate agents were octafluoro-2-butene, HFC-236fa, octafluoro-2-butene/1-bromopropane (93:7 mass ratio), and HFC-236fa/1-bromopropane (88:12 mass ratio). HFC-236fa was selected as an agent simulant to conserve the amount of octafluoro-2-butene consumed (HFC-236fa has thermophysical properties similar to octafluoro-2-butene).

Several different extinguishers were used during the fire suppression tests. Halon 1211 was discharged from a standard Halon 1211 extinguisher. The candidate agents were discharged from an Ansul<sup>®</sup> model CA-1481 fire extinguisher, designed for use with HFC-236fa agent. This extinguisher has a UL Rating of 2-A:10-BC. Three Ansul extinguishers were used. Extinguisher 0 was an unmodified extinguisher. Extinguisher 1 was modified by opening the hose and valve orifice flow areas 15.9% and 17.1%, respectively. Extinguisher 2 was modified by opening the hose and valve flow areas 25.1% and 31.9%, respectively. The extinguisher modifications were performed to allow for increased agent flow rates.

Table 1 and Figures 1 and 2 summarize the test results. Figures 1 and 2 show that octafluoro-2-butene, HFC-236fa, and their blends with 1-bromopropane (nbp) required more agent, required higher agent discharge rates, and had higher discharge times than Halon 1211 for successful extinguishment. Discharge rates for octafluoro-2-butene, HFC-236fa, and their blends ranged from approximately 0.9 lbs/sec to 1.8 lbs/sec, compared to about 0.9 lbs/sec for Halon 1211. Successful extinguishment required 6-12 lbs. of the candidate agents, compared to 5 lbs for Halon 1211. Successful extinguishment was achieved in 6-12 seconds for the candidate agents,

compared to 5 seconds for Halon 1211 (less than 8 seconds is a UL requirement). Lower discharge rates for the candidate agents were not successful in extinguishing the fire.

**Table 1. Results of Fire Suppression Tests.**

Agent	N <sub>2</sub> Pres. (psig)	Extinguisher	Discharge Time (sec)	Amount (lbs.)	Application Rate (lbs/sec)	Application Density (lbs/ft <sup>2</sup> -min)	Fire Out
Halon 1211		Halon 1211	5	4.7	0.94	2.26	yes
HFC-236fa	75	0		12.7	<1		no
HFC-236fa	75	0			<1		
HFC-236fa		0	9.1	8.7	0.96	2.29	yes
HFC-236fa		0	6.1	7.1	1.16	2.79	yes
HFC-236fa	75	0		14.6	<1		no
HFC-236fa	75	0	8.4	13	1.55	3.71	yes
HFC-236fa/nbp	75	0	16.1	13.9	0.86	2.07	no
HFC-236fa/nbp	75	0	20	14.4	0.72	1.73	no
HFC-236fa/nbp	75	0	20	14	0.70	1.68	no
HFC-236fa/nbp	125	0	16	14.3	0.89	2.15	no
HFC-236fa/nbp	195	0	25	20.2	0.81	1.94	no
HFC-236fa/nbp		0	12.1	14.4	1.19	2.86	no
HFC-236fa	75	0	12.1	12.1	1.00	2.40	yes
2-Butene	75	0	15.8	14.6	0.92	2.22	no
2-Butene	125	0	8.7	10.9	1.25	3.01	yes
2-Butene	125	0	9	9.8	1.09	2.61	yes
2-Butene	125	0	15.3	14.7	0.96	2.31	no
2-Butene	125	0	15	14.8	0.99	2.37	no
2-Butene	125	0	15	15.1	1.01	2.42	no
2-Butene	150	0	17	17	1.00	2.40	no
2-Butene/nbp	125	0	8.5	11	1.29	3.11	yes
2-Butene/nbp	125	0	15.6	15.1	0.97	2.32	no
HFC-236fa/nbp	75	2	12.5	14.4	1.15	2.76	yes
HFC-236fa/nbp	75	2	14.9	12.6	0.85	2.03	no
HFC-236fa	75	0	16	12.2	0.76	1.83	yes
2-Butene	125	2	10	14.5	1.45	3.48	no
2-Butene	75	2	15	14.6	0.97	2.34	no
2-Butene	100	2	12.8	14.5	1.13	2.72	no
2-Butene	125	0	14	14.9	1.06	2.55	no
2-Butene/nbp	125	2	6.75	12.3	1.82	4.37	yes
2-Butene/nbp	125	2	6.87	12.6	1.83	4.40	yes
2-Butene/nbp	125	1	12	15.1	1.26	3.02	no

Flow Rate Versus Discharge Time

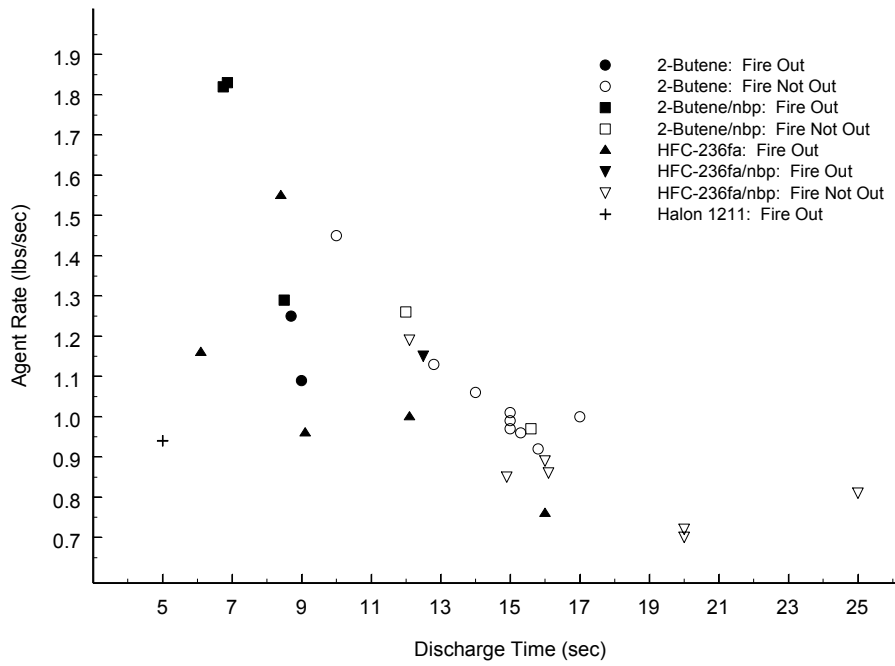


Figure 1. Agent discharge rate versus discharge time.

Flow Rate Versus Agent Amount

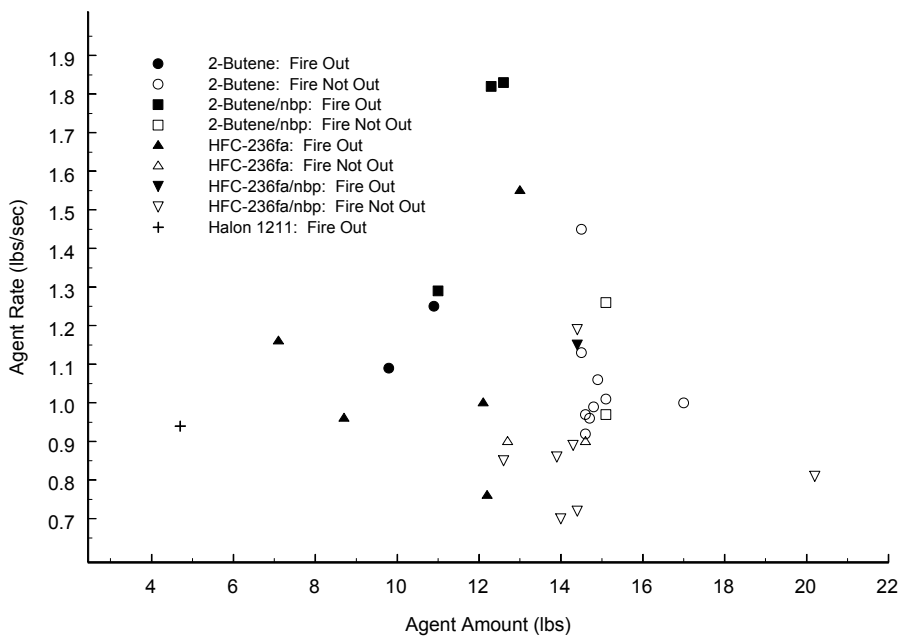


Figure 2. Agent discharge rate versus amount of agent discharge.

Firefighter technique played a significant role in fire extinguishment. Typically, the firefighter would apply the agent to the front of the pan in a sweeping motion, and push the fire to the rear of the pan until the fire is extinguished. There were several tests where the fire was very close to being extinguished near the rear the fire pan, only to burn back and re-ignite the fuel at the front of the pan. This may explain some of the scatter in the data and the overlap of “fire out” and “fire not out” data points.

The fire suppression test data shows that the addition of 1-bromopropane to either octafluoro-2-butene or HFC-236fa had marginal, if any, performance benefits. Both octafluoro-2-butene and HFC-236fa were able to extinguish the fires using lower application rates and with less agent, than when blended with 1-bromopropane. The HFC-236fa/1-bromopropane blend was only able to extinguish the fire 1 out of the 8 times tested.

The fire suppression data obtained on this program can be compared to data obtained by others with the same agents on the same size fire. Moore and Lifke (Ref. 2) performed fire suppression testing on 25 ft<sup>2</sup> jet fuel fires with UL-10B extinguishers. They evaluated Halon 1211, HFC-236fa, and the HFC-236fa/1-bromopropane blend. A comparison of the data obtained on this program with the data of Moore and Lifke is presented in Table 2. The data generated on this program and the data of Moore and Lifke are in general agreement except for the HFC-236fa/1-bromopropane tests, where poorer performance was obtained than that of Moore and Lifke.

**Table 2. Comparison of Fire Suppression Data**

<b>Agent</b>	<b>These Data</b>	<b>Data of Moore and Lifke</b>
Halon 1211		
Extinguishment Time (sec)	5	4.8
Extinguishment Amount (lbs)	4.7	3.12
Application Rate (lb/sec)	0.94	0.65
HFC-236fa		
Extinguishment Time (sec)	6.1 - 16	8 – 10
Extinguishment Amount (lbs)	7.1 - 13	9.1
Application Rate (lb/sec)	0.76 – 1.55	1.0
HFC-236fa/1-bromopropane		
Extinguishment Time (sec)	12.5	6 – 10
Extinguishment Amount (lbs)	14.4	5.4 - 7.5
Application Rate (lb/sec)	1.15	0.73 - 1.1

The data from this project can also be compared to the data generated in Phase I of this program (Refs 3-4) to see how well the minimum application density scales from a 0.43 ft<sup>2</sup> heptane pan fire to a 25 ft<sup>2</sup> JP-8 pan fire. Table 3 presents this comparison. Table 4 shows that the minimum application densities are similar for neat octafluoro-2-butene and HFC-236fa, but are significantly different for the agent blends.

**Table 3. Comparison of Small-Scale and Large-Scale Fire Suppression Data.**

<b>Agent</b>	<b>Small-Scale Minimum Application Density (lb/ft<sup>2</sup>-min)</b>	<b>Large-Scale Minimum Application Density (lb/ft<sup>2</sup>-min)</b>
octafluoro-2-butene	2.3 – 2.6	2.6
octafluoro-2-butene/1-bromopropane	1.5	3.1
HFC-236fa	1.65 – 1.8	1.8
HFC-236fa/1-bromopropane	1.6	2.8

**TOXICITY INFORMATION**

Table 2 compares the acute inhalation toxicity information of octafluoro-2-butene and 1-bromopropane with some other fire suppression agents and refrigerants. Table 4 shows that octafluoro-2-butene has a slightly higher acute inhalation toxicity than the other agents listed.

**Table 4. Acute Inhalation Toxicity Data (Rat).**

<b>Common Name</b>	<b>15 min LC<sub>50</sub> (ppm)</b>	<b>4 hr LC<sub>50</sub> (ppm)</b>	<b>Comments</b>
Halon 1211	200,000	31-131,000	
Halon 1301	> 800,000	> 800,000	
CFC-11	130-150,000	26,200	
CFC-12	> 800,000	> 800,000	
CF <sub>3</sub> I	270,000	~160,000	4 hrs. @ 128,000: no deaths 4 hrs. @ 200,000: 100% death
octafluoro-2-butene	> 90,000	~5750	4 hrs. @ 5400: no deaths 4 hrs. @ 6100: 100% deaths 1 hr @ 14,000: no deaths
1-bromopropane	~ 100,000 (time/conc. extrap.)	Not Available	30 min LC <sub>50</sub> = 50,432 ppm

Table 5 presents genotoxicity information on octafluoro-2-butene and other agents and refrigerants. Octafluoro-2-butene compares favorably to the other agents in the Table.

Huntingdon Life Sciences performed cardiotoxicity studies on octafluoro-2-butene and a 93:7 (w/w) blend of octafluoro-2-butene and 1-bromopropane. A sample of 100% octafluoro-2-butene was administered at concentrations of 3.0%, 4.0%, 5.0%, 7.0%, and 9.0% (vol./vol.) in air. There was no evidence of cardiac sensitization at concentrations up to and including 9.0%. However, three of the four dogs exposed at 9% expired within 48 hours of exposure; the cause of death is unknown but is considered to be attributable to the exposure. The study concluded that

octafluoro-2-butene does not cause cardiac sensitization in beagle dogs up to 9% (vol./vol.) but does appear to cause fatalities following exposure at 9%. The mechanism for this is not known. Thus, the NOAEL for octafluoro-2-butene is 7.0% and the LOAEL is 9.0%. A mixture of 93 wt% octafluoro-2-butene and 7 wt% 1-bromopropane was administered at concentrations of 0.95%, 2.03%, 3.11%, 3.93%, 4.80%, and 7.09% (vol./vol.) in air. There was no evidence of cardiac sensitization at concentrations up to and including 3.93%. Two dogs had a positive response at 4.80%. The remaining four dogs were exposed at 4.80% and 7.09% with no positive responses. Thus, a NOAEL of 3.93% and LOAEL of 4.80% have been established for the 93:7 (wt./wt.) blend of octafluoro-2-butene/1-bromopropane.. Table 6 summarizes this information and compares the agents to other tested agents and refrigerants. Table 6 shows that most of the other agents are more potent cardiac sensitizers than octafluoro-2-butene.

**Table 5 - Genotoxicity Data**

<b>Common Name</b>	<b>In Vitro Bacteria (Ames)</b>	<b>In Vitro Mammalian Cells</b>	<b>In Vivo Micronucleus (mouse)</b>
Halon 1211	Positive (1/5 strains)	Negative	50,000 ppm NOAEL (6 hrs/day x 3 days)
Halon 1301	Negative	Not Available	Not Available
CFC-11	Negative	Negative	Not Available
CFC-12	Negative	Negative	Not Available
CF <sub>3</sub> I	Positive (4/5 strains)	Negative	25,000 ppm NOAEL 50,000 ppm LOAEL (6 hrs/day x 3 days)
octafluoro-2-butene	Negative	Negative at 5,000 ppm Positive ≥ 50,000 ppm	Negative at 300 and 600 ppm (6 hrs/day x 2 days)

**Table 6. Cardiac Sensitization Data.**

<b>Common Name</b>	<b>NOAEL (ppm)</b>	<b>LOAEL (ppm)</b>	<b>Comments</b>
Halon 1211	5,000	10,000	EC50 = 19,000 ppm
Halon 1301	50,000	75,000	EC50 = 200,000 ppm
CFC-11	3,200	3,500	EC50 = 9,000 ppm
CFC-12	40,000	50,000	EC50 = 77,000 ppm
CF <sub>3</sub> I	2,000	4,000	
octafluoro-2-butene	70,000	90,000	3 of 4 dogs exposed at 90,000 ppm expired within 48 hours of exposure
93% octafluoro-2-butene/ 7% 1-bromopropane	39,300	48,000	

## ATMOSPHERIC IMPACT

The ODP of octafluoro-2-butene is zero. In order to assess the atmospheric lifetime of octafluoro-2-butene, researchers at NIST (Ref 2) measured the rate constant for the reaction between hydroxyl radicals and octafluoro-2-butene over the temperature range of 230-480 K. The rate constant showed very little temperature dependence. The measured rate constant at the atmospherically important temperatures of 298 K and 272 K is (Ref. 5):

$$k (298 \text{ K}) = (5.11 \pm 0.3) \times 10^{-13} \text{ cm}^3/\text{molecule-sec}$$

$$k (272 \text{ K}) = (5.27 \pm 0.3) \times 10^{-13} \text{ cm}^3/\text{molecule-sec}$$

Based on the measured reactivity of octafluoro-2-butene towards hydroxyl radicals, its atmospheric lifetime was estimated by NIST researchers to be as short as 25 days (Ref. 5). Because its atmospheric lifetime is so low, its GWP is also expected to be very low.

That atmospheric properties of 1-bromopropane are well-documented.

## MATERIALS COMPATABILITY

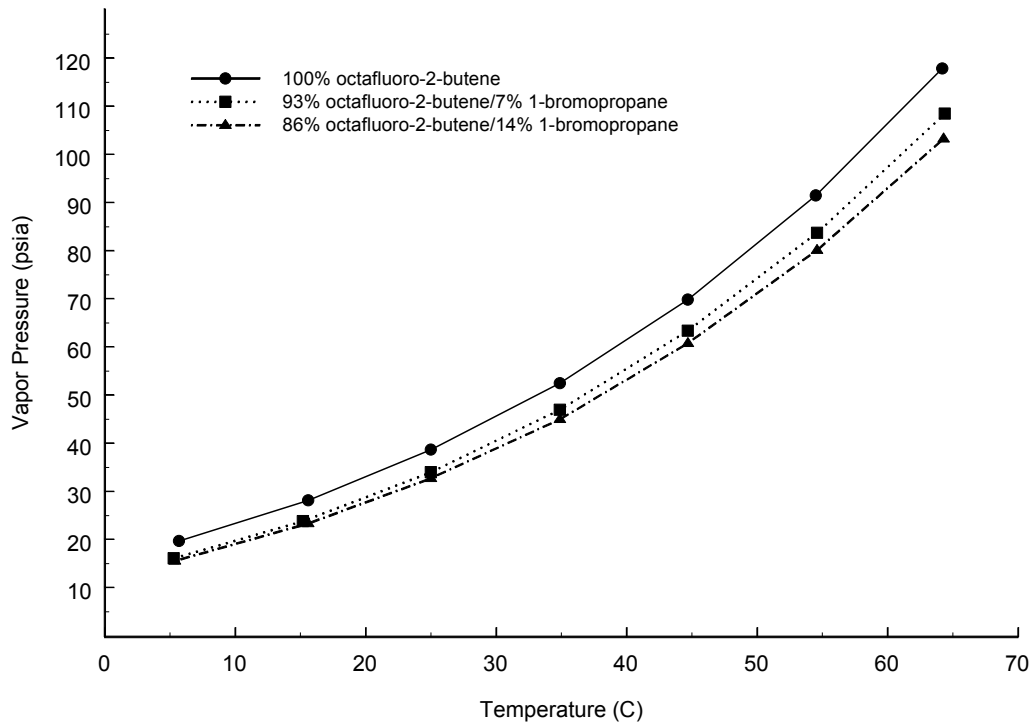
Materials compatibility experiments were performed with octafluoro-2-butene, Halon 1211, and 93:7 (w/w) and 86:14 (w/w) mixtures of octafluoro-2-butene and 1-bromopropane using modified ASTM Methods (Refs 6-7). The metals tested were aluminum 2024, copper CDA 260, copper CDA 110, stainless steel 304L, 1020 carbon steel, and Inconel 600. Elastomers tested were Buna N, EPDM-60, neoprene, silicon rubber, Teflon, and Viton A. Materials compatibility tests indicated that octafluoro-2-butene was compatible with all metals evaluated, and had less of an affect on the elastomers evaluated than Halon 1211 did. The complete test results are presented in Reference 1.

## DECOMPOSITION PRODUCT ANALYSIS

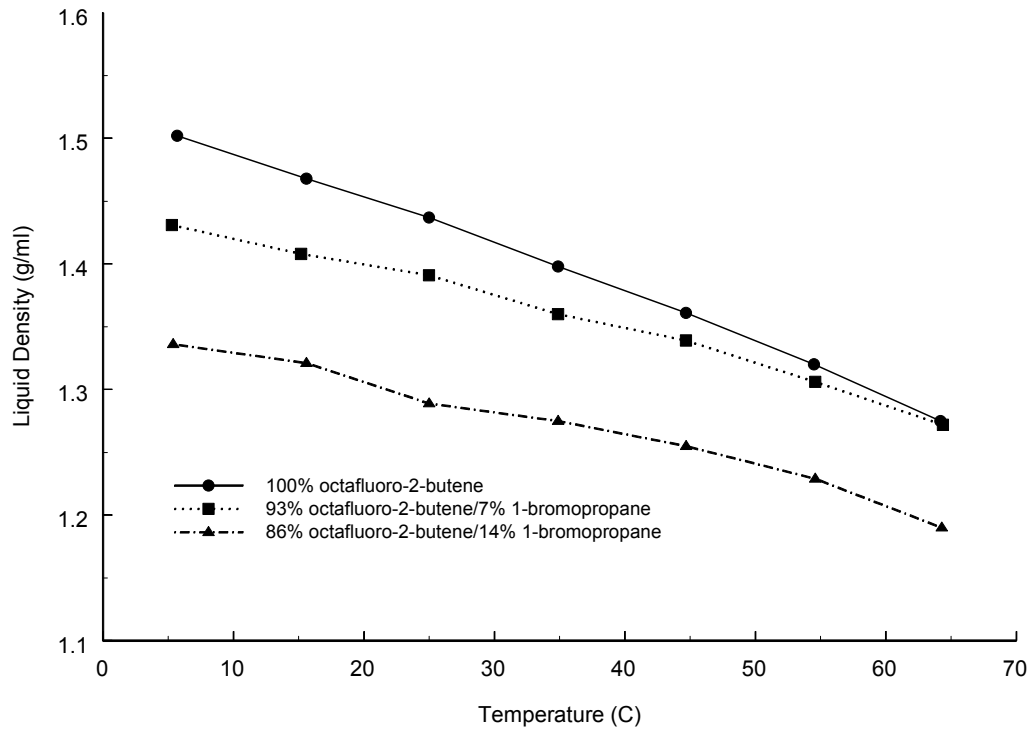
Agent decomposition analysis of octafluoro-2-butene showed it generated low levels of acid gases (HF), but no toxic perfluoroisobutene decomposition product was detected. Mixtures of octafluoro-2-butene with 1-bromopropane showed much higher levels of decomposition, at lower temperatures, than octafluoro-2-butene alone. The decomposition products detected for those mixtures contained both fluoride and bromide ions. The complete test results are presented in Reference 1.

## THERMOPHYSICAL PROPERTIES

The thermophysical properties of octafluoro-2-butene and mixtures if 1-bromopropane in octafluoro-2-butene in the 0-20% range were measured using methods described in Reference 8. The vapor pressure, liquid density, liquid viscosity, and surface tension of these agents were measured in the 5-65°C range; see Figures 3-6. Nitrogen solubility was measured at various nitrogen pressures using the method of Yang (Ref. 9). The 1-bromopropane /octafluoro-2-butene mixtures had lower nitrogen solubility than pure octafluoro-2-butene. Table 7 presents these results. Reference 1 contains the complete thermophysical property characterizations.

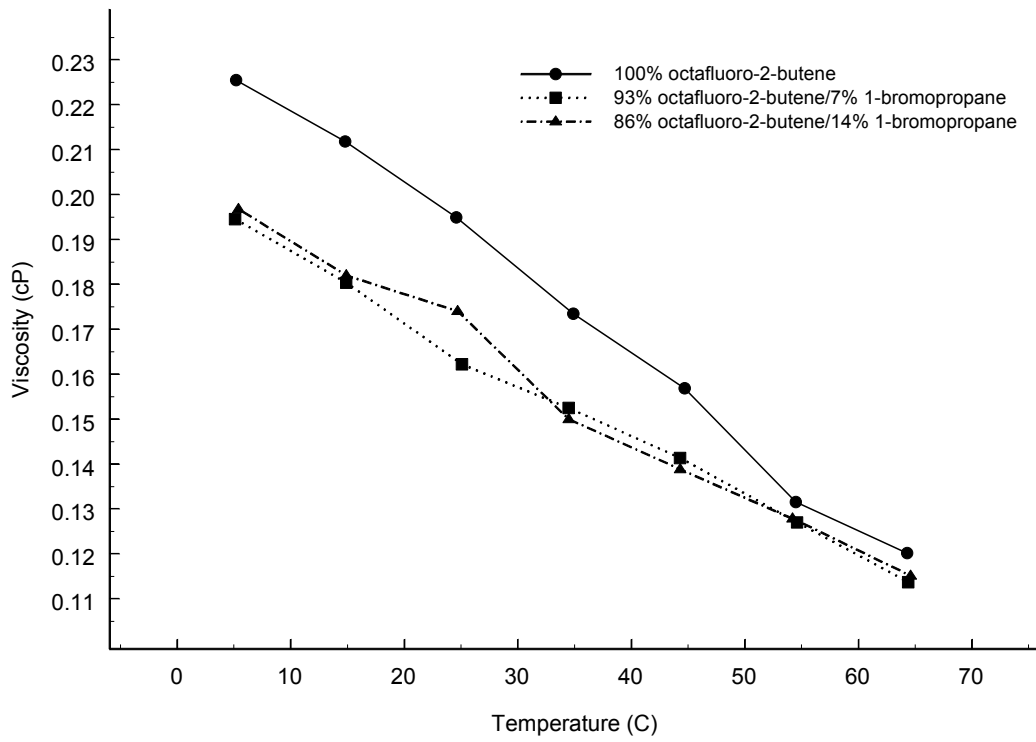


**Figure 3. Agent vapor pressure measurements.**

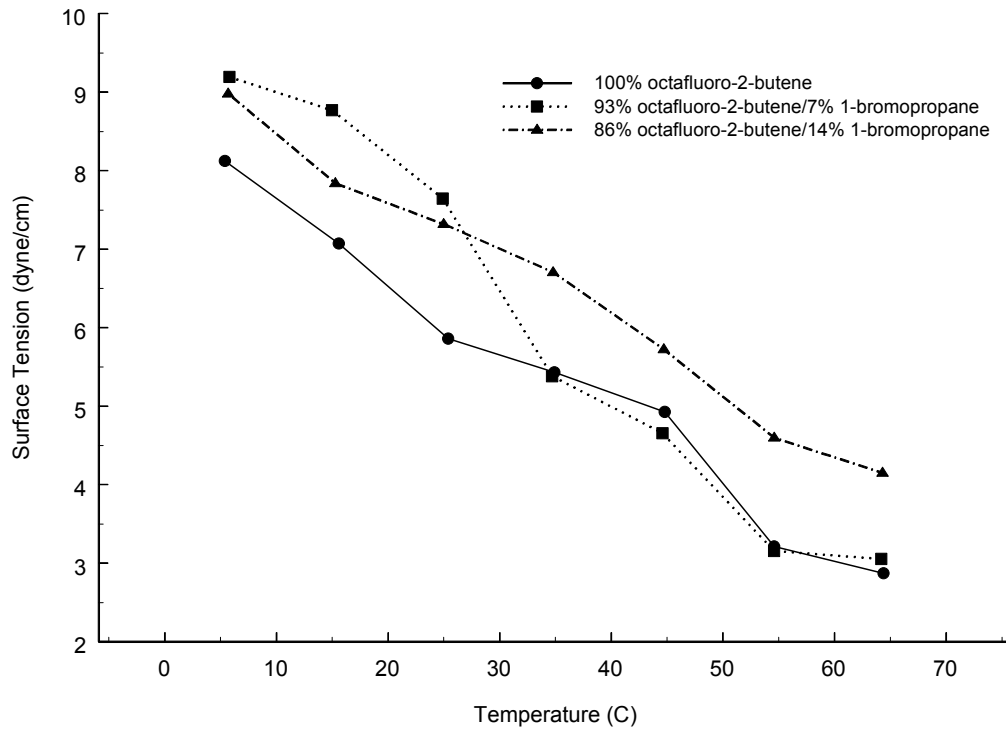


**Figure 4. Agent liquid density measurements.**





**Figure 5. Agent viscosity measurements.**



**Figure 6. Agent surface tension measurements.**

**Table 7. Nitrogen Solubility Measurements.**

<b>Temperature (°C)</b>	<b>Pressure (psia)</b>	<b>Mole Fraction N<sub>2</sub></b>	<b>Mass Fraction N<sub>2</sub></b>
<i>100% octafluoro-2-butene</i>			
25.3	75.2	0.285	0.053
25.3	150.2	0.368	0.075
25.3	300.2	0.389	0.082
<i>93% octafluoro-2-butene/7% 1-bromopropane</i>			
25.3	75.2	0.216	0.039
25.3	150.3	0.313	0.062
25.3	300.1	0.302	0.060
<i>86% octafluoro-2-butene/14% 1-bromopropane</i>			
25.3	75.0	0.159	0.028
25.3	150.1	0.263	0.052
25.3	300.2	0.269	0.053

### **ASSESSING AGENT MANUFACTURING**

SynQuest Laboratories provided 300 lbs. of octafluoro-2-butene at a cost of \$525/lb. Purity was stated as 98.4%. Synquest uses a proprietary pilot-plant process to produce octafluoro-2-butene. They provided a rough order of magnitude estimate for larger scale production. For 10,000 lbs, they estimate the price to be \$100/lb using the pilot-plant process. For quantities larger than 10,000 lbs. a continuous process would be used, which would require some process development work and the building of a suitable facility (an expensive undertaking). However, they estimate pricing in the \$40-50/lb. for quantities of less than 200,000 lbs. and \$20-40/lb. for quantities over 200,000 lbs.

### **CONCLUSIONS**

Octafluoro-2-butene has the potential to be a substitute for Halon 1211 and HFC-236fa for streaming fire suppression applications. It does require more agent, higher agent discharge rates, and higher discharge times than Halon 1211 for successful extinguishment, but has the same fire suppression performance as HFC-236fa. Also, the fire suppression tests showed that the addition of 1-bromopropane to either octafluoro-2-butene or HFC-236fa had marginal, if any, performance benefits.

Octafluoro-2-butene does not have the atmospheric impact of either Halon 1211 or HFC-236fa. Octafluoro-2-butene has zero ODP, low atmospheric lifetime, and low GWP. HFC-236fa has zero ODP but a high atmospheric lifetime and high GWP. Halon 1211 is a known ozone depleter with high GWP.

The toxicity information developed on this project indicate that more subchronic and long-term toxicity information is required for octafluoro-2-butene. It does not appear to be as potent of a cardiac sensitizer as other fire suppression agents or refrigerants, but it did appear to cause lethality in dogs after exposure to 9% agent in air. The cause for these lethalties also needs to be evaluated.

Materials compatibility tests indicated that octafluoro-2-butene was compatible with all metals evaluated, and had less of an affect on the elastomers evaluated than Halon 1211 did. Agent decomposition analysis showed it generated low levels of acid gases (HF), but no PFIB decomposition product was detected.

For octafluoro-2-butene to be a commercial fire suppression agent, more work on manufacturability needs to be performed. Specifically, the cost of the agent needs to be significantly reduced, to the range of \$20-40/lb. Initial estimates of the cost of manufacturing in large quantities, in a continuous process, show that this cost reduction is feasible with some process development work and the building of a suitable plant.

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