TROPODEGRADABLE BROMOCARBON EXTINGUISHANTS
—PROGRESS OVERVIEW—

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INTRODUCTION

In work most recently sponsored by the DoD Next-Generation Fire Suppression Technology Program (NGP), research efforts at The University of New Mexico have been evaluating chemical agents as substitutes for Halons 1301 and 1211. This effort has been focused entirely on a new class of compounds referred to as tropodegradable bromocarbons. Testing results to date are very favorable, and there is strong indication that, as a group, the tropodegradable bromocarbons may well yield acceptable replacements for both Halon 1301 and 1211. Past research work on new total-flood and streaming agents has established the potential of tropodegradable bromocarbons as fire suppressants; however, flame extinguishment experiments were insufficient to relate performance (and, for some compounds) flammability to structure [1 through 5]. NMERI's recent NGP project was conceived in part to address the need for more laboratory-scale fire extinuishment information on tropodegradable compounds. Several tropodegradable candidate compounds have been identified from the alkene, ether, and amine families. Acquisition of promising compounds to date has been primarily from the alkene and amine families.

This report summarizes the past years acquisition, extinguishment and toxicology studies on tropodegradable bromocarbon extinguishants. The inhalation toxicity studies were performed under financial support from the **US** Air Force (Tyndall AFB) [6], the Next-Generation Program (NIST) [1], and the Advanced Agent Working group (AAWG). The Ames toxicity study reported here was performed by the Advanced Agent Working Group [6]. The report also covers current efforts to identify acquire and test additional tropodegradable compounds as well as screening techniques developed for performing cup-burner testing ***of*** small quantities of compound.

EARLY DEVELOPMENT EFFORTS

Commercialized halon replacements such as perfluorocarbons (PFC, FC), hydrochlorofluorocarbons (HCFC), hydrofluorocarbons (HFC), hydrofluoropolyethers (HFPE), and iodofluorocarbons (CF_3I) do not contain bromine. With the exception of CF_3I, all current commercialized halon replacements have much higher air concentration requirements for cup-burner flame extinguishment. This is largely attributable to the absence of bromine in the structures of these chemicals. All current commercialized halon replacements, except CF_3I, are significantly less effective in many scenarios than halons and exhibit long atmospheric lifetimes and high global warming potentials.

In recent years two approaches to reintroducing bromine into fire suppressants have been tested. The first approach is based on the use of blends of bromoalkanes with HFCs or HFPEs. This approach, when compared to the performance of neat HFC or HFPE, does result in enhanced cup-burner flame extinguishment performance and streaming performance. The blend technology is currently being evaluated for commercialization. The second approach taken to reintroducing bromine into the fire suppression agent takes advantage of compounds with intrinsically very low atmospheric lifetimes (on the order of days or weeks) to act as a carrier or base structure to which a bromine atom is added (Table 1). Such compounds are said to be tropodegradable because for all practical purposes they rapidly and completely degrade within the troposphere and never reach the stratosphere or the earth's ozone layer. When bromine is contained within the molecular structure of a short atmospheric lifetime compound, the resulting chemical is referred to a tropodegradable bromocarbon. The carrier compounds generally are only partially fluorinated and incorporate chemical features that are reactive with atmospheric •OH or O_3 or that are inherently polar such as alcohols and therefore subject to atmospheric removal by the rainout process. CF_3I's inclusion as a tropodegradable compound arises from photolysis of the C-I bond as a result of exposure to sunlight.

TABLE 1. TROPODEGRADABLE CARRIERS AND BROMINATED DERIVATIVES.

Tropodegradable Base Structure	Tropodegradable Bromocarbon Derivative
$CH_2=CHCF_3$	$CH_2=CBrCF_3$, $CHBr=CHCF_3$
$CH_2=CFCF_3$	$CHBr=CFCF_3$
$CH_2=CFCF_2H$	$CH_2=CHCF_2Br$, $CHBr=CFCF_2H$
$CHF=CHCF_3$	$CFBr=CHCF_3$, $CHF=CBrCF_3$

Tropodegradable compound atmospheric lifetimes have in some cases been measured but generally are estimated based on data generated for functional groups such as sites of unsaturation, numbers of C-H bonds, and substitution patterns. Early estimates of atmospheric lifetime for alkenes, which were as low as a few days, have now been demonstrated to be accurate." Amines are estimated to have atmospheric lifetimes on the order of one or more months. Ethers are estimated to have atmospheric lifetimes of days to months. The brominated ether CH_3OCF_2 CHFBr (commonly known as Rotluorane) has been reported to have an to have atmospheric lifetime of 14 days [7].

The reactions that cause atmospheric decomposition of a molecule differ for alkenes, ethers, and amines. For alkenes reaction with hydroxyl free radicals or with tropospheric or ground level ozone are expected to target the double bond while ethers and amines would be subject to hydrogen abstraction reactions by the •OH radical. Photolysis of the C-I bond is the predominant reaction pathway for iodinated fluoroalkanes such as (CF_3I). Direct physical removal of alcohols through rainout is not contingent on the reactivity of the compound.

RESEARCH ON TROPODEGRADABLE FIRE SUPPRESSANTS AT NMERI

Concerted efforts to advance the research on tropodegradable bromocarbons as replacements for Halons 1211 and 1301 began several years ago and continue to the present. Halon 1301 replacement work involving the evaluation of tropodegradable bromocarbons has received the bulk of its past funding by the Next-Generation Program (NGP) and by the Advanced Agent Working Group (AAWG). Halon 1211 replacement work has been funded exclusively by the US Air Force (Tyndall AFB). Additional funders who have contributed to these compound selection, acquisition and testing projects include the US Army TACOM, US Navy, Federal Aviation Administration (FAA), and Environmental Protection Agency (EPA).

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* Vladimir Orkin, personal communication, NIST *(41612000)*.

A research strategy was developed early in these projects to govern the selection of compounds for acquisition and identification of relevant testing. This strategy is based on information gathered or estimates made on the types of compounds under consideration as **well** as individual compounds. Information gathered included estimates of atmospheric lifetime and ozone depletion potential (ODP), global warming potential (GWP), various toxicity end points, physical properties (e.g., boiling point vapor pressure, density, etc), and estimates of cup-burner flame extinguishment for Halon 1301 replacement candidates and streaming agent performance for Halon 1211 replacement candidates.

All of these research programs addressed the problem of selecting appropriate toxicity end points and developing a ranking of their relative importance. This information became part of the basis for the preliminary screening prior to actual acquisition and or synthesis efforts. Table 2 presents an example of the selection criteria developed early in the Halon 1211 replacement program.

Functional upper limits on compound boiling point for total flood, and to a lesser degree streaming agent applications were estimated. In the case of total-flood agents vapor pressure under the conditions of usage are seen as a primary factor in the fire *or* explosion performance of an agent. Estimates of theoretical ambient vapor pressure as a function of boiling point and ambient temperature (based on Trouton's constant) are summarized in Table ***3***. From this chart it can be estimated that for a compound to achieve a 4% air concentration at -40 °C, it must have boiling point no greater than ***31*** °C. Where application conditions are –10 °C the permitted boiling point limit is higher at 70 "C. This estimate says nothing about the time required to establish the targeted air concentration.

TABLE 2. HALON 1211 REPLACEMENT CANDIDATE CRITERIA.

Criteria	Value
Boiling Point	< ~ 80 °C
LC_{50}* (4-hr)	> 50,000 ppm (5.0%)
Cup-bumer performance	< 5.0%
ODP	<0.02
GWP	< 5,000
Atmospheric Lifetime	< 5 years
Cardiac Sensitization (CS_{NOAEL})	> 2 times the FEC
Cleanliness	No solid residue
Application density	Similar to that of Halon 1211 in a 5 **by** 5-ft n-heptane pan fire test.

*Lowest concentration causing death in 50% of an animal test population.

TABLE 3. ESTIMATES OF MAXIMUM USEABLE BOILING POINTS

Conc.	Ambient Temperature, °C											
%	-60	-50	-40	-30	-20	-10	0	10	20	30	40	50
1	33	47	61	76	YO	105	119	133	148	162	176	191
2	19	33	46	60	74	87	101	115	128	142	156	169
3	11	24	31	51	64	77	91	104	117	130	144	157
4	5	18	31	44	57	70	83	96	109	122	135	148
5	0	13	26	39	52	65	77	90	103	116	129	142
10	-14	-1	11	23	35	41	59	72	84	96	10X	120
15	-22	-10	2	14	25	*31*	49	61	73	X4	Y6	10X
20	-28	-16	-5	7	19	30	42	53	65	76	88	99

Example: To achieve a 4 vol% concentration at –20 °C, the maximum allowable boiling point is 57 "C.

The pivotal criteria that evolved through extensive evaluations and eventually formed **a** basis for selection and evaluation of compounds as either Halon 1301 or 1211 replacement candidates are summarized in Table 4.

TABLE 4. SELECTION PARAMETERS.

Parameter estimated or determined	Halon 1211 replacement candidate	Halon 1301 replacement candidate
Fire Suppression Performance	NMERI LSDE (Streaming test)	Cup-Burner (NMERI)
Environmental	Atmospheric Lifetime, ODP, GWP	Atmospheric Lifetime, ODP, GWP
Toxicity	Acute inhalation, Ames test (mutagenisity), carcinogenicity, cardiac sensitization	Acute inhalation, Ames test (mutagenicity), carcinogenicity, cardiac sensitization
Physical Properties	Boiling point, vapor pressure	Boiling point, vapor pressure

Based on an analysis of atmospheric reactivity various chemical families were selected. The chemical families expected to exhibit short(er) atmospheric lifetimes and therefore provide the basis for developing tropodegradable bromocarbon extinguishants are listed below.

- Brominated alkenes
- Brominated ethers
- Brominated alkyl amines
- Brominated alcohols
- Brominated aromatics
- Brominated carboxylates

Of these chemical families, the brominated alkenes, ethers, and amines were judged the most likely to meet desired boiling point restrictions, environmental, and toxicity goals. Of these three families, the bromofluoroalkenes were judged the most favorable. Toxicity requirements are generally viewed as presenting the most difficult hurdle in the development of a halon replacement.

Extensive toxicity information for many candidate compounds and chemical families was gathered and evaluated early in the halon replacement program. Published toxicity data for the building block molecule 3,3,3-trifluoropropene, indicating an LC_{50} of 430,676 ppm, was particularly favorable and suggested the possibility of developing an acceptable brominated derivatives.* One such brominated derivative of 3,3,3-trifluoropropene is 2-Bromo-3,3,3-trifluoropropene (boiling point 34 °C). This compound in fact had been used in inhalation testing involving dogs where the test animals were reported to recover uneventfully from the exposure [5]. Unfortunately no concentration data was provided for this test. Toxicity data for the bromofluorobutene, 4-bromo-3,3,4,4-tetrafluorobutenes indicated a 4-hour ALC in rats greater than 19,300 ppm. This compound has also been found not to be mutagenic in Ames bacterial assay or clastogenic in Chinese Hamster Ovary (CHO) cell assay.

To date the list of bromofluoroalkenes acquired for which cup-burner flame extinguishment has been characterized is presented in Table 5. The data all indicate that regardless of compound structure, straight chain or branched, and propene, butene, or pentene derivative the flame extinguishment is generally below 4% with most of the tested compounds yielding cup-burner values comparable to Halons 1301 and 1211. Only when the degree of fluorination falls to less than 50% of available positions (total of number of H's, fluorines and bromines) does the cup-burner value rise significantly above 4%.

Testing of the streaming performance of tropodegradable bromofluoroalkenes is very limited. Data from a laboratory scale streaming agent test apparatus have been acquired. Figure 1 shows the relative performance of several experimental compounds, commercial agents, and the tropodegradables 2-bromo-3,3,3-trifluoropropene and 4-bromo-3,3,4,4-tetrafluorobutene compared to Halon 1211. The test evaluates agent application rates vs fire out times. As can be seen from the chart, the compound 2-bromo-3,3,3-trifluoropropenes fire suppression performance approximates that of Halon 1211.

Acute inhalation toxicity testing was performed last year on a limited selection of tropodegradable compounds representing a range of molecular weights, boiling points, and structural features. The list of compounds represented both straight chain molecules as well as branched molecules, and to a limited extent, structural isomers such as 2-bromo-3,3,3-trifluoropropene and 1-bromo-3,3,3-trifluoropropene were evaluated. The test exposure protocol called for a 30-min exposure of 10 rats (5 male and 5 female) to each individual chemical at an air concentration of 5%. Following the exposure the animals were removed from the exposure apparatus. observed for 2 hours, then sacrificed for examination of tissues. This testing was part of a project being performed under **US Air** Force funding to develop a replacement for the streaming agent Halon 1211 [6]. The toxicity testing program received additional funding and support from the AAWG, US Army (TACOM), and US Navy.

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*Lawrence **R.** Grzyll, Mainstream Engineering Corporation, personal communication, April 1997.

TABLE 5. BROMINATED TROPODEGRADABLE HALOCARBON CUP-BURNER VALUES.

CCOD ID	Compound, Formula	Boiling Pt (°C)	Cup-burner (%)
707	***1-Bromo-3,3,3-trifluoropropene, $CF_3CH=CHBr$***	***40***	***3.5****
872	3-Bromo-3,3-difluoropropene, $CBrF_2CH=CH_2$	42	4.5
873	***2-Bromo-3,3,3-trifluoropropene, $CF_3CBr=CH_2$***	***34***	***2.6***
903	***4-Bromo-3,3,4,4-tetrafluorobutene, $CF_2BrCF_2CH=CH_2$***	***54***	***3.5***
1116	***2-Bromo-3,3,4,4,4-pentafluorobutene, $CF_3CF_2CBr=CH_2$***	***56***	***3.8"***
1358	2-Bromo-?,3,4,4,5,5,5-heptafluoropentene, $CF_3CF_2CF_2CBr=CH_2$	78	3.7*
1359	2-Bromo-3-trifluoromethyl-3,4,4,4-tetrafluorobutene, $CF_3CF(CF_3)CBr=CH_2$	78	3.3"
1360	2-Bromo-3-trifluoromethoxy-3,4,4,4-tetrafluorobutene, $CF_3CF(OCF_3)CBr=CH_2$	75	3.8"
1391	1-Bromo-2-trifluoromethyl-3,3,3-trifluoropropene, $(CF_3)_2C=CHBr$	63	2.6*
1413	1-Bromo-4,4,4,3,3-pentafluorobutene, $CF_3CF_2CH=CHBr$	58	3.1*

"Testing performed using premixed agent/air mixtures.

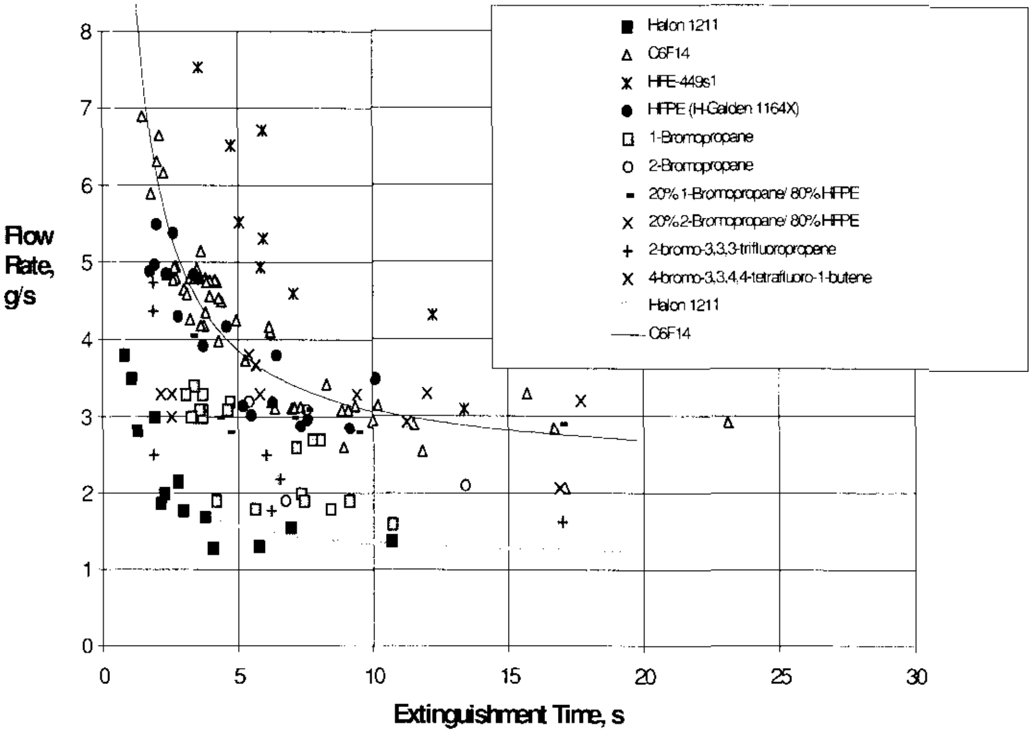

Figure 1. Comparative laboratory streaming agent test results.

Some of the results of this exposure testing are presented below in Table 6. Shown are the mortality/survivability for each chemical used in the exposure program as well as lung tissue observations made following animal sacrifice. A surprising number of the test compounds produced no mortality or lung tissue damage. Those compounds having the least impact on the test animals also had the lowest boiling points. Selected exposure observations made during the acute inhalation toxicity test and the two hour post exposure observation period are listed below in Table 7. The observations presented are for three of the compounds selected for continued evaluation.

TABLE 6. ACUTE INHALATION TOXICITY TESTING.

CCOD ID	Formula	Number of Rat Deaths	Lung Tissue Observations (at necropsy)
873	CH_2=$CBrCF_3$	0	All rat tissues normal
707	$CHBr$=$CHCF_3$	0	All rat tissues normal
872	CH_2=$CHCBrF_2$	7	Lungs were mottled
903	CH_2=$CHCF_2CBrF_2$	0	All rat tissues normal
1116	CH_2=$CBrCF_2CF_3$	0	Lungs were mottled
1360	CH_2=$CBr(OCF_3)CFCF_3$	10	Lungs were mottled
1358	CH_2=$CBrCF_2CF_2CF_3$	1 **(post** exposure)	Lungs were mottled
1359	CH_2=$CBrCFC(CF_3)_2$	10	Lungs had marked mottling

Organ weight and weight ratios reflected the post exposure observations (Table 8). Compound 1116 is described as resulting in the following post-exposure effects "labored breathing continued to 20 min post-exposure. Respiration continued in this manner until sacrifice." This observation is reflected in the average lung weights for animals exposed to Compound 1116, which are more than twice those of the control group. Tissue weights for Compounds 873,707, and 903 are statistically the same as those of the control group by comparison.

Following these successful tests of acute inhalation toxicity, the AAWG performed testing of Ames mutagenicity on three of the more readily available compounds. The results of the testing, which was performed by DuPont, are presented in Table 9. All three compounds tested negative in this test indicating that they are not mutagenic.

As presented in this review, tropodegradable bromofluoroalkenes have been demonstrated to be effective fire extinguishants in both streaming and total-flood applications. Cup-burner data indicate that for compounds where the degree of fluorination is equal to or greater than 50%, the extinguishment concentrations are as low as 2.6%. Boiling points for many of the compounds acquired range from 34 to 74 °C. Testing of the performance of these compounds in actual fire and explosion suppression tests at sub-ambient temperature conditions is needed to assess performance. Toxicity testing results are very promising and further testing is planned in the near future. Atmospheric Lifetimes data reported during the HOTWC 2000 meeting confirmed the short lifetime estimates of a few days for the tropodegradable bromofluoralkenes.

TABLE 7. ACUTE INHALATION TOXICITY TESTING EXPOSURE OBSERVATIONS.

Exposure Test Group	Observations
Controls:	Normal during 30 min exposure. Occasional movement in tubes. Good pink color of extremities with normal respiration. Upon being unloaded rats appeared normal and begin grooming themselves.
Compound 873:	Relaxed breathing began shortly after exposure. Little movement within tubes within first few minutes then none thereafter. Animals appeared to be anesthetized. After exposure animals were anesthetized for a few minutes then began moving about although with impaired motor activity. Back to normal after about 10 min post-exposure, and normal throughout to sacrifice.
Compound 903:	At 12 min of exposure color was good, breathing relaxed, and there was no movement indicating the rats were anesthetized. Animals remained this way throughout exposure. After exposure rats remained anesthetized for 2-3 min then began waking. Rats were stumbling around by 5 min post-exposure and were very wobbly. By 20 min post-exposure all rats appeared normal and continued normally until sacrifice.
Compound 1116:	At 3 min into exposure respiration was irregular, and became labored with gasping by 8 min. At 13 min respiration was slowed and animals appeared to be anesthetized. By 20 min F058 (animal number) was breathing very slowly, paws were pale purple indicating insufficient oxygenation. By 5 min post-exposure rats were waking and had labored breathing: labored breathing continued to 20 min post-exposure. Respiration continued in this manner until sacrifice.

TABLE 8. ACUTE INHALATION TOXICITY TESTING ORGAN WEIGHT OBSERVATIONS.

Organ	Control	Compound 873	Compound 707	Compound 903	Compound 1116
Lungs	0.962	0.980	1.007	1.054	2.211
Kidneys	1.527	1.509	1.605	1.608	1.747
Spleen	0.506	0.544	0.573	0.545	0.514
Heart	0.658	0.696	0.692	0.716	0.715
Lung/body ratio	0.429	0.438	0.442	0.452	0.943

TABLE 9. AMES MUTAGENICITY TEST RESULTS

CCOD ID	Compound. Formula	Ames Test Result
873	2-Bromo-3,3,3-trifluoropropene, $CF_3CBr=CH_2$	Negative
903	4-Bromo-3,3,4,4-tetrafluorobutene, $CF_2BrCF_2CH=CH_2$	Negative
1116	2-Bromo-3,3,4,4,4-pentafluorobutene, $CF_3CF_2CBr=CH_2$	Negative

Limited testing of tropodegradable amines has also been performed. Several of the bromofluoroamines acquired are listed in Table 10. Though the compounds acquired have excellent cup-burner flame extinguishment performance, their boiling points may make them unsuitable for anything but streaming applications. Additional bromofluoroamines with lower boiling points are being sought for testing as Halon 1301 replacements.

Polyfluoroamines and polyfluorobromoamines listed in Table 11 give hope that this chemical family may yet yield additional compounds with boiling points as low as 20 to *30* °C. Based on testing of perfluorinated amines expectations are that the acute inhalation toxicity of bromofluoroamines may be low.

TABLE 10. TROPODEGRADABLE BROMOFLUOROAMNES.

CCOD ID**	Compound, Formula	Boiling pt °C	Cup-burner (%)
1392	Bis(trifluoromethyl)-2-bromo-1,2,2-trifluoroethyl amine, $N(CF_3)_2(CHFCF_2Br)$	12	2.4"
1393	Bis(trifluoromethyl)-2-bromo-1,1,2-trifluoroethyl amine, $N(CF_3)_2(CF_2CFHBr)$	12	
1398	Bis(trifluoromethyl)-2-bromo-2-fluoroethylamine, $N(CF_3)_2(CH_2CF_2Br)$	80	2.4

* Results of a 60/40 blend of CCOD's 1392 and 1393
** NMERI Chemical Compound Options Database ID

TABLE 11. POLYFLUOROAMNE BOILING PONTS.

Formula	Boiling point, °C (°F)
$N(CF_3)_3$	-10
$(CF_3)_2NCF{=}CF_2$	13.7
$(CF_3)_2NCF_2CF_3$	20 to 22
$(CF_3)_2NCF_2CHF_2$	32.0
$(CF_3)_2NCBrF_2$	40.6
$(CF_3)_2NCF_2CBrF_2$	59.5 to 60.5
$N(CF_2CF_3)_3$	70.3

CONCLUSION

Overall the compound search has had very positive results. Bromofluoroalkenes as a class have exhibited considerable promise as potential halon replacements and further acquisition of compounds related to 2-bromo-3,3,3-trifluoropropene and 4-bromo-3,3,4,4-tetrafluorobutene will likely lead to the identification of additional low boiling candidates. Continued acquisition and testing programs will also include studies of bromofluoroethers and to a lesser extent bromofluoroamines as these two classes of compounds have shown promise in the limited testing performed.

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