NGP SEARCH FOR NEW CHEMICALS - ENVIRONMENTALY ACCEPTABLE FIRE SUPPRESSANTS

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HALON REPLACEMENT PROGRAM EFFORTS

As the NGP program began in the mid 1990's it is useful to include a limited review of knowledge gained as a result of efforts that occurred in the years prior to the NGP. Changes in thinking occurred frequently in the early 1990's amongst those involved in identifying and evaluating new fire suppressant compounds. Realization that instead of a single drop-in replacement being identified for halon 1301 (as well as halon 1211) the world of fire suppression applications was going to see a broad range of new agents and technologies. Criteria for environmental acceptability changed significantly during this period, risk assessment based toxicity tests and limits were identified, and understanding of situational toxicological constraints underwent considerable evolution.

Halon 1301 is unique as a brominated fluorocarbon. Its -58 °C boiling point is the lowest of the bromofluoroalkane chemical family. Its toxicity is quite low and it is an excellent fire suppressant and explosion inertant. Its low boiling point and excellent fire suppression properties give it great dimensionality (space filling), tolerance to less than optimal discharge technique, and excellent long term chemical stability. As a consequence the search for alternatives based on higher boiling compounds (basically all other conceivable chemical extinguishants) faced a considerable challenge to even come close to matching the overall performance of halon 1301.

With the emphasis on dramatic reductions in both stratospheric ozone depletion effects and atmospheric global warming potentials one research focus has been on identifying short atmospheric lifetime molecules. Short atmospheric compounds incorporate structural components that are reactive with atmospheric constituents of the atmosphere or are photochemically reactive, Table 1.

TABLE 1. TROPOSPHERIC REMOVAL MECHANISMS

Primary removal mechanism	Example families
Photodegradation	Iodides, Carbonyls, Bromides
Reaction with Hydroxyl	Alkenes, Aromatics, Hydrogen-Containing Amines, Hydrogen-Containing Ethers, Carbonyls
Physical Removal	Ketones, Alcohols, Esters
Reaction with Tropospheric Ozone	Alkenes

In the 1970's work on fire suppressants performed at the Naval Research Laboratory studied a variety of fire suppression related topics and potential chemicals agents including SF_5/CH_4 and a number of other compounds.[1,2] Research at NRL also studied CF3I flame extinguishment[3,4] and conducted studies of hydrogen fluoride (HF) byproduct formation resulting from halon 1301 fire extinguishment.[5,6]

Efforts funded by the US Air Force at NMERI sought replacements for halon 1211. Early NMERI work on streaming agent replacements for halon 1211 funded research led to development of methods of estimating atmospheric lifetime and ozone depletion,[7] laboratory scale test methods,[8] methods for evaluation of materials compatibility and operational validation,9 and preliminary lists of advanced agents (chemically active suppressants).[10]

Early U. S. Air Force (USAF) sponsored research at NMERI on "first-generation" (CFCs and HFCs) halon replacement candidates focused on chemicals that were or soon would be readily available and that had a significant amount of known toxicological information.[11]

HCFCs will eventually be phased out of production due to their non-zero ODP, and some restrictions are already in place in parts of Europe (and to a limited extent in the USA). The European Community (EC) regulation 3093/94, which entered into force on 1 June 1995, does not allow the use of HCFCs for fire protection. HFCs had been prominent as replacements for ozone depleting substances but, in 1996 Denmark announced that they planed to phase out all hydrofluorocarbons (HFCs) within the next 10 years due to global warming.[12]

Under US Air Force sponsorship the National Institute of Standards and Technology published in August 1990 NIST Technical Note 1279.[13] This report is titled "Construction of an Exploratory List of Chemicals to Initiate the Search for Halon Alternatives." This report was the first systematic survey since late 1940's of chemical families potentials as halon replacements. The report identified a range of specific chemical families with potential as sources of halon replacement and provided listing of 103 compounds of immediate interest for further testing in flame extinguishment and explosion suppression.

TABLE 2. NIST LIST OF RECOMMENDED CHEMICAL FAMILIES (1990)

Chemical family recommendation	Justification for further consideration - Environmental advantage and flame suppression estimates
Halogenated ketones, anhydrides, esters	Carbonyl red shift contributes to photolysis
Unsaturated halocarbons	Reactivity of alkenes to atmospheric OH
Halogenated ethers and related compounds	Absorption red shift due to C-O-C linkage aides in photolysis
Halons containing iodine	Iodinated halogenated compounds more photochemically reactive and a higher fire suppression efficiency
Sulfur halides	Desirable attributes - Low toxicity, possible significant fire suppression properties
Phosphorus containing compounds	Established fire suppression properties (expected free radical trap mechanism) needs a more volatile or gaseous compound
Silicon and germanium compounds	Silicon in particular (possibly germanium) expected flame suppression effectiveness and short atmospheric lifetime
Metallic compounds	Established flame suppression properties, likely alternative compounds of great interest
Inert gases	Physical suppressant options

Guiding attributes required of a replacement halon included: fire suppression effectiveness, low residue level, low electrical conductivity, low metals corrosion, high materials compatibility, stability under long term storage, low toxicity (inhalation and contact) of the chemical and its combustion products, and low (or zero) contributions to stratospheric ozone depletion and global warming. The report summarized the various mechanisms of flame extinguishment and listed approaches to altering a chemical to decrease its contribution to ozone depletion including enhancement of agent/chemical reactivity with atmospheric •OH radicals.

This study provided a useful guide for halon researchers in the early 1990's. In fact, several of the chemical families identified as well as approaches to selecting environmentally acceptable short atmospheric lifetime compounds identified were successfully employed in later studies.

The Halon Options Technical Working Conference held its first annual meeting in the spring of 1991. The conference continues to the date of this publication as a forum for presentation of research related to halon replacements and as such routinely covers topics ranging from new agents and fire suppression equipment to atmospheric science and chemical and suppression by-product toxicology.

The DoD's Technology Development Plan (TDP) was initiated to identify alternatives for fire extinguishment in occupied spaces by 1997 under Technical Plans I-VI. The plans covered RDT&E activities performed by the Navy and one by the Air Force with the goal of identifying alternative chemicals, processes and/or techniques for extinguishment fires in occupied compartments.

The AAWG was formed in August 1994 by representatives of most DoD services, NIST, EPA, several fire suppression industry representatives, private consultants, and the New Mexico

Engineering Research Institute (NMERI). The AAWG in work funded some of the initial efforts to determine the probability of identifying clean advanced agents for use in normally occupied areas. A listing of specific chemicals was developed for study which emphasized estimated short atmospheric lifetime and the presence of bromine in the chemical structure. Toxicological and physical property reviews of this list of compounds were performed. Little cardiac sensitization data could be identified at this point and models in existence did not address essential toxicological end points such as cardiac sensitization. U.S. Army Center for Health Promotion and Preventative Medicine (CHPPM) employed TOPKAT to model QSAR toxicity predictions.14 British Ministry of Defence (MOD) DERA employed DEREK (Deductive Estimation of Risk from Existing Knowledge version 15.1)[15], to evaluate the same list of compounds.

Inhalation exposure acute toxicity testing at 5 vol. percent, Table 3, of eight bromofluoro alkenes demonstrated no adverse effects in the five of the tested compounds.[16]

TABLE 3. ACUTE INHALATION TOXICITY TROPODEGRADABLE BROMOFLUOROALKENES

Compound	Formula	Deaths[a] during (post) exposure
1-Bromo-3,3,3-trifluoropropene	$CF_3CH{=}CHBr$	0
2-Bromo-3,3,3-trifluoropropene	$CF_3CBr{=}CH_2$	0
4-Bromo-3,3,4,4-tetrafluorobutene	$CF_2BrCF_2CH{=}CH_2$	0
2-Bromo-3,3,4,4,4-pentafluorobutene	$CF_3CF_2CBr{=}CH2$	0
2-Bromo-3,3,4,4,5,5,5-heptafluoropentene	$CF_3CF_2CF_2CBr{=}CH_2$	0 (1)
3-Bromo-3,3-difluoropropene	$CH_2{=}CHCBrF_2$	7
2-Bromo-3-trifluoromethoxy-3,4,4,4-tetrafluorobutene	$CH_2{=}CBr(OCF_3)CFCF_3$	10
2-Bromo-3-trifluoromethyl-3,4,4,4-tetrafluorobutene	$CH_2{=}CBrCFC(CF_3)_2$	10

a 10 rats and a 30-minute exposure at 5% v/v agent air concentrations

The surprisingly good results from this round of acute inhalation testing provided impetus for a greatly expanded program of testing for selected bromofluoroalkenes. The AAWG provided the funding for this and many of the other toxicity testing efforts mentioned here. The Ames Mutagenicity test results[17] on the more promising compounds selected based on boiling point were equally reassuring as were the results of the chromosomal aberration tests.[18] Cardiac sensitization testing of two bomofluoropropenes was performed.[19,20] While the 1 % LOAEL value observed for 2-bromo-3,3,3-trifluoropropene is disappointingly low and the compound not useable as a halon 1301 replacement, the compound may well be able to serve as a halon 1211 replacement, usable in unoccupied areas.

While the limited toxicity data are promising, increased fluorination of these molecules is desirable in order to obtain reduced boiling points. It is unclear where the optimum in degree and pattern of fluorination and site of bromination lies. Given the many additional compounds that have yet to be tested hope that at least one will have acceptable cardiac sensitization and other toxicity properties to be acceptable for use in occupied areas does not seem entirely unreasonable.

The status of alternative agents and development of selection criteria prior to the start of NGP research efforts was dominated by non-brominated fluorocarbons and dry powder extinguishants. An almost universal goal of all researchers was the demand by the halon user community for a drop-in replacement agent. This goal is defined as the identification of a new environmentally acceptable agent that enabled users to retain all their current halon systems (storage bottles, piping, valves, and nozzles) while matching or exceeding halon 1301 in it low toxicity and superior fire suppression performance and fire fighting dimensionality.

The development of CF_3I reached a critical point prior to the start of the NGP with the announced results of cardiac sensitization LOAEL performance far lower than that of even halon 1211. Use of CF_3I was questioned and additional risk assessments performed. The broad applicability of the highly aggressive dog exposure based agent and epinephrine challenge for assessment of cardiac sensitization was questioned. Overall though the lack of a useable screening method for cardiac sensitization represented a major financial barrier to the candidate chemical selection process.

Incorporating bromine in short atmospheric lifetime (tropodegradable) compounds as a means of achieving more aggressive flame suppression and hopefully reducing agent weight requirements was a well recognized option. Potentially tropodegradable compounds possessing molecular features susceptible to attack by atmospheric •OH or •H radicals or tropospheric ozone, photolysis by solar radiation, hydrolysis by atmospheric moisture, or simply polar enough to dissolve in rain in a process referred to as rain out were reviewed extensively. In all cases compounds considered retained fluorine in their molecular structures in order to achieve non-flammability and to reduce boiling points.

NGP PROGRAM – NEW CHEMICALS SCREENING

A very broadly scoped review and analysis of chemical family's potential and known suitability for study is summarized in NIST Technical Note 1443.[21] The goal of this review was to identify chemical families still in need of scrutiny as potential flame suppressants and halon replacements, to list those chemical families for which sufficient knowledge exists to select the best candidates and finally to identify those families unlikely to contain useable alternative fire suppressing chemicals.

Compounds with particularly good flame extinguishment characteristics as reflected by their having low extinguishment concentration requirements can have proportionately higher boiling points. Flame suppression enhancing compounds amenable to use in high temperature dispersion systems such as pyrogenically generated aerosols or solid propellant gas generator types of fire suppression systems can have considerably higher boiling points than agents whose dispersion requires vaporization under ambient temperatures. The conclusion of the review was a categorization into "High Priority", "Further Study", and "Quick Look" classifications for the Chemical families found to be of interest, Table 4.

TABLE 4. CHEMICAL FAMILIES SELECTED FOR CONSIDERATION

Chemical Family	Recommendation		
	High Priority	Further Study	Quick Look
Iodine-containing alkanes		X	
Iodine-containing alkenes		X	
Bromine-containing alkenes	X		
Iodine-containing ethers			X
Bromine-containing ethers		X	
Bromine-containing alcohols			X
Fluorine-containing aldehydes and ketones		X	
Nitriles			X
Fluoro- and bromofluoroamines	X		
Sulfoxides			X
Phosphorus-containing Acids and Esters	X		X
Phosphonitriles		X	
Phosphorus halides		X	
Copper-containing Compounds			X
Manganese-containing Compounds	X		
Iron-containing compounds		X	
Tin-containing compounds	X		

All families studied were evaluated in terms of predicted fire suppressant properties, toxicity, colligative properties, environmental and atmospheric impact, and materials compatibility. These families in some cases had been well characterized and no additional study of their properties was needed. Other chemical families exhibited toxicities that were clearly outside all reasonable limits. In some cases the chemical families colligative properties rendered the likelihood of dispersion remote or there was simply no reason to suspect that the chemical family possessed chemical flame extinguishment properties that were significant that would justify the cost and effort involved in further consideration.

CHEMICAL PROPERTIES AND ENVIRONMENTAL SUITABILITY ESTIMATION

The toxicities, physical properties, Ozone Depletion Potentials (ODP), and Global Warming Potentials (GWP) of chemical that might be appropriate for halon 1301 applications were reviewed and/or estimated. Reference 22 gives an overview of global environmental problems and presents a detailed discussion of ODP, GWP, the various tropospheric removal mechanisms, and approximation methods. Estimation techniques included Quantitative Structure Activity Relationships for toxicity; estimated or known hydroxyl free radical rate constants with globally averaged atmospheric hydroxyl radical concentrations for lifetimes; estimation methods for conversion of lifetimes to ODP and GWP based on data fitting to known values; and estimation of physical removal and photolytic removal based on chemical and physical properties. Sources of toxicity and safety data employed in these efforts included Sax and Lewis and the Registry of Toxic Effects of Chemical Substances (RTECS).[23,24]

Down-selecting chemicals benefits greatly from the existence of low cost readily available test methods as well as the chemical(s) of interest. Unfortunately neither of these was the case. Cardiac sensitization testing proved extremely expensive and no screening method was ever proven through testing. Candidate methods were identified. These included reverse phase high pressure liquid chromatography (RP-HPLC) and gas chromatography mass-spectrometry methods which are employed in the assessment of environmental toxicity and pharmaceutical activity and effect. The RP- HPLC (and GCMS) method employs compounds for which KOW values are known and compares chromatographic retention time data for unknown compounds to that of the known compounds. KOW values for unknowns are derived directly form this data. Both methods require only nanogram or milligram quantities of compound. These methods require only mg of compound and provide easy means for the selection of additional promising compounds.

The approach may provide a method for estimating cardiac sensitization for a series of compounds. The result could be a ranking of compounds, identification of compounds with expected higher LOAEL values and facilitation of compound acquisition.[22,25]

NGP - CHEMICAL FAMILY SURVEYS

The search for alternative fire suppressants and in particular, replacements for halon 1301, was broad in scope. To ensure that the most optimal chemicals were identified a comprehensive search and assessment of a broad array of chemical families and elements was performed.

- Main Group Elements of Groups IA, IIA, IIIB, IVB, VB, VIB, VIIB, and VIIIB
- Bromofluoro-Alkenes
- Fluoroalkoxide and Fluoroalkyl Phosphorus Compounds
- Bromofluoro Amines
- Bromofluoro Ethers

NGP LOW BOILING POINT - FOCUSED STUDIES OF CHEMICAL FAMILIES

The focus on aircraft applications necessitated a strong emphasis on identifying low boiling suppressant chemical families and individual chemicals. Consideration for possible superior extinguishment performance broadened the search by inclusion of some chemical families thought to be potential sources of highly effective suppressant compounds. The chemical families studied and specific chemicals identified and in some cases acquired and evaluated by cup-burner are described.

Fluoroalkoxide and Fluoroalkyl Phosphorus Compounds

A focused study of fluoroalkyl phosphorus compounds in which eight compounds were identified and seven ultimately acquired and tested provided detailed information on flame suppression, air reactivity, boiling point trends and also aided in the identification of additional compounds which were estimated to be effective extinguishants. Unfortunately, as the observed flame extinguishment performance was not indicative of an enhanced performance (< 3vol.%) and because the boiling points for these compounds were above the cut-off they were not included in the continued search for low boiling environmentally acceptable extinguishants.

Low Boiling Environmentally Acceptable Extinguishants

The low temperature conditions experienced by aircraft whether located in extreme climates or in flight at altitude greatly impact selection of chemical agents and their methods of discharge. Identifying new chemical agents for aircraft necessitated a focused study of low boiling compounds with the potential to serve as replacements. An extensive research evaluation was performed in order to identify specific chemical families and chemicals for further study and development.[26] While earlier studied had also identified and characterized several low boiling compounds most of their efforts were confided to the bromofluoroalkenes and ethers.

Employing NIST Technical Note 1443 as guidance, Table 4, chemical families that were likely to represent low boiling candidate compounds were selected for study. Additional chemical families were included based on structural or functional similarities to known flame extinguishing compounds where examination indicated the possible tropodegradability. The combined list of chemical families served as the focus of compound acquisition and extinguishment testing.

TABLE 5. POTENTIALLY LOW BOILING CHEMICAL FAMILIES

Chemical family
Bromofluoro propenes and ethenes
Bromofluoro dimethyl ethers and methyl ethyl ethers
Bromofluoromethylamines and n-Bromofluoromethylamines
Bromofluoroimines
Bromofluoropropene oxides (oxiranes)
Bromofluoro acetonitriles

While some estimates of fire suppression application needs are as low as -60 °C more recent analysis seem to suggest that application temperatures in the -20 °C range could be more representative of actual aircraft fire suppression application needs.

Regardless of the chemical family under consideration low boiling points are easiest achieved by keeping molecular weight to a minimum while avoiding flammability of the compound. These goals are somewhat in opposition as non-flammability can only be achieved through sufficient, usually 50%, substitution of fluorine for hydrogens in the molecular structure. Too much fluorination in a molecule, while generally but not always imparting a lower boiling point and decreased flammability can result in increased atmospheric lifetimes. This is an issue that affects ethers in particular.

Low Boiling - Bromofluoro Alkenes

With the focus on the lowest boiling alkenes the direction of compound acquisition and testing focused primarily on the tetrafluoro and pentafluoro bromopropenes and selected isomers of brominated difluoroethenes thought based on the chlorinated analogues to not be flammable. The chemical family of bromofluoropropenes represents an extensive array of structural possibilities. The tetrafluorinated and pentafluorinated bromopropenes alone represent 17 unique compounds some of which are *cis* (Z) and *trans* (E) isomers of one another. Extinguishment studies also included the nonflammable compound 1-bromo-1,2-difluoroethene, CFBr=CFH.

Several of these compounds were acquired and their cup-burner extinguishment evaluated, Table 6 1-bromo-1,2-difluoroethene cup-burner extinguishment performance of 8.4 vol.% is outside the desired range for continued consideration and as such completes the study of the low boiling bromofluoroethenes. The tetra and pentafluoro bromopropenes are clearly the lowest boiling chemical suppressants in the alkene family.

TABLE 6. LOW BOILING BROMOFLUORO ALKENE CUP-BURNER VALUES

Compound	Boiling Point (°C)	Cup-Burner Extinguishment (vol.%)
1-Bromo-pentafluoropropene	27	3.1
2-Bromo-pentafluoropropene	25	3.5
3-Bromo-1,1,3,3-tetrafluoropropene	33	3.3
2-Bromo-1,3,3,3-tetrafluoropropene	29	3.5
2-Bromo-1,1,3,3-tetrafluoropropene	29	3.3
1-Bromo-2,3,3,3-tetrafluoropropene	30 (est.)	3.3
2-Bromo-3,3,3-trifluoropropene	32-34	3.1
1-Bromo-1,2-difluoroethene	20 – 24 (est.)	8.4

Trifluorinated, tetrafluorinated and pentafluorinated bromopropenes all are good extinguishants with no indications of flammability.

Low Boiling Bromofluoro Ethers

Two early studies of fire suppression by of the higher boiling hydrobromofluoroethers (HBFEs) have been carried out. $CH_2=CBr(OCF_3)CF_2CF_3$ which is unsaturated, has a cup burner extinguishment concentration of 3.8 volume percent. CH_3-O-CF_2CHBrF (also known as the anesthetic Roflurane) has been estimated to have a heptane cup burner volume fraction of 4.2 % and a short atmospheric lifetime.[27]

With the focus on low boiling compounds consideration shifted to a limited number of bromofluoro methyl ethyl ethers,

With the focus on low boiling compounds brominated fluorodimethyl ethers were of greatest interest. These compounds have been sought on several occasions with limited success. Following a review of prior attempts and literature and unpublished synthetic details both bromomethyltrifluoromethyl ether and bromomethyldifluoromethyl ether were eventually obtained. Extingusihement testing of both compounds by cup-burner provided flame extinguishment data characteristic of chemically active agents. Cup-burner performance and boiling points for CH_2Br-O-CF_3, (39-41 °C) 3.2% and bromomethyl difluoromethyl ether, CH_2Br-O-CF_2H, (70 °C) 3.6% are promising,

Table **8**. Substituting additional fluorine for a hydrogen on CH_2Br-O-CF_3 may yield a compound (two structural isomer are possible) with a boiling point in the vicinity of 20 to 30 °C suggesting that additional fluorination is worth a try. Ethers may well have superior long term materials stability with respect to the alkenes.

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Table 7. Bromofluoro methyl ethyl ether Cup-Burner Testing Summary

Compound, Formula	Boiling point, (°C)	Cup-Burner Extinguishment (vol.%)
1-Bromo-1,2,2-trifluoroethyl trifluoromethyl ether, $CF_3OCFBrCF_2H$	42	$<^{c}$ 4.5
2-Bromo-1,1,2-trifluoroethyl trifluoromethyl ether, $CF_3OCHFCF_2Br$	37	< 4.5

TABLE 8. BROMINATED FLUORO DIMETHYL-ETHER FLAME EXTINGUISHMENT DATA

Compound	Formula	Boiling Point, °C	Cup-Burner
Bromomethyl trifluoromethyl ether	$CH_2Br-O-CF_3$	39	3.2%
Bromomethyl difluoromethyl ether	$CH_2Br-O-CF_2H$	70	3.6%
Bromodifluoromethyl difluoromethyl ether	$CF_2Br-O-CF_2H^{a}$	20-24 (est.)	3.7 (2.4)[b]

a Impure sample 65% bromodifluoromethyl difluoromethyl ether, 25 % bisdifluoromethyl ether, 10% other ethers
b Estimated extinguishment value based on a 65% purity
c < signify upper limit extinguishment value.

The cup-burner extinguishment performance of the sample of 65% bromodifluoromethyl difluoromethyl ether was ether was initially calculated as if the sample were 100% pure. If the observed 3.7 % extinguishment value is corrected for the actual 65% purity of the sample an extinguishment value of 2.4% is obtained. It is unlikely that the major impurity in this sample (bisdifluoromethyl ether) contributes significantly to extinguishment at its effective low concentration of 0.9%. The remaining impurities in this sample included predominantly chlorinated analogues to the desired product.

Based on these results the ether bromofluoromethyl trifluoromethyl ether (CFHBr-O-CF3) would also be of interest unfortunately however sources of the required fluoroether starting material (CFH2-O-CF3) could not be located.

Bromofluoro ethers exhibit some of the lowest boiling points of any of the compounds tested. The toxicity of ethers is relatively low and the ether linkage has a relatively low biological and chemical reactivity. There are an abundant number of structural isomers and boiling points to a low of 20 to 24 °C appear to be possible. Limited atmospheric lifetime estimates[27] suggest the possibility of acceptable performance over a range of many of these compounds.

Low Boiling Bromofluoro Propene Oxides

The propene oxides (or oxiranes) were expected to be low boiling compounds. As carriers of bromine there was potential for them to exhibit acceptable flame extinguishment properties as well. Testing indicates that perfluoropropene oxide has a cup-burner value of 9.6 vol.%.[28] Toxicity is unknown. These compounds are expected to be stable under storage and may be readily attached by OH radicals. Their atmospheric lifetimes may well be short, but this is unconfirmed. Synthesis of 3-bromopentafluorooxirane has been reported.[29,30] $CF_2(O)CBrCF3$ (2-bromo-1,2-perfluoropropene oxide) was successfully sourced and flame extinguishment of 4.9 vol.% determined Given the unspectacular cup-burner results further investigation of the bromofluoropropene oxides was halted.

Low Boiling Bromo and N-Bromo fluoro Amines, Imines and Nitriles

Bromofluoro amines have been studied previously however the boiling points of acquired compounds representing bromine and fluorine substituted dimethyl ethyl amines were well outside acceptable volatility limits, Table 9.

Table 9. Bromofluoroamine Cup-Burner Flame Extinguishment Data

Compound, Formula	Boiling point °C	Cup-burner (%)
Bis(trifluoromethyl)-2-bromo-1,2,2-trifluoroethyl amine, $N(CF_3)_2(CHFCF_2Br)$	72	2.4[a]
Bis(trifluoromethyl)-2-bromo-1,1,2-trifluoroethyl amine, $N(CF_3)_2(CF_2CFHBr)$	72	
Bis(trifluoromethyl)-2-bromo-2-fluoroethylamine, $N(CF_3)_2(CH_2CF_2Br)$	80	2.4

a Results of a 60/40 blend of $N(CF_3)_2(CHFCF_2Br)$ and $N(CF_3)_2(CF_2CFHBr)$

Bromofluoro nitriles as well as the related n-brominated amines, imines and nitriles were until recently unstudied. This is in large measure due to a lack of availability of starting materials and facilities willing to attempt the chemistry. Synthetic approaches to some compounds have been developed and reported.[31,32,33] Several compounds from these chemical families may well have boiling points low enough to warrant further study confirmation. Two of the compounds have been reported and their boiling points determined. The two reported compounds n-bromobistrifluoromethylamine, ($(CF_3)_2N$-Br, 22 ºC) and N-bromo-difluoromethanimine, (CF_2=NBr, boiling point 14 ºC) have attractively low boiling points as does the compound bromodifluoroacetonitrile, (CF_2BrCN, boiling point 3 ºC). These compounds may be unacceptable toxic but that is as yet unconfirmed. As possibly environmentally acceptable compounds with boiling points lower than 30 C are rare, interest in pursuing the synthesis of these two compounds as well as other related bromofluoro and n-brominated amines, imines, and nitriles, was attempted.

The related and readily available compounds bromodifluoroacetonitrile (CF_2BrCN), boiling point 3 ºC) and trifluoroacetonitrile, ((CF_3CN), boiling point -64 ºC) were also of interest due to their rather low boiling points and utility as a means of evaluating the effects of triple bonds on flame extinguishment.

TABLE 10. CUP-BURNER EXTINGUISHMENT OF NITROGEN BASED EXTINGUISHANTS

Compound	Boiling point, (°C)	Cup-burner Extinguishment (vol. %)
N-Bromo-difluoromethanimine, $CF_2=NBr$	14	a
N-Bromobistrifluoromethylamine, $(CF_3)_2N\text{-}Br$	22	a
Bromodifluoroacetonitrile, CF_2BrCN	3	< 4%
Trifluoroacetonitrile, CF_3CN	-64	9%

a Compound synthesis incomplete

It was considered unlikely that nitriles would have an intrinsic (chemical) fire suppression capability and this was verified in these studies. Nonhalogenated nitriles are known or are expected to be flammable. Fluorination is likely to reduce flammability and these compounds are likely to be physical suppressants. The addition of bromine or iodine would impart a chemical flame suppression property.

CF_3CN has an extremely low boiling point and might possibly be a tropodegradable compound. CF_2BrCN is also a low boiling brominated compound and potentially tropodegradable. Cup-burner testing of both compounds was performed.

CF_2BrCN demonstrated the enhanced extinguishment expected of a brominated compound and indicated little adverse effect from the presence of the CN group however it should be emphasized that it may be quite toxic. The high required exitinguishment concentreation of CF_3CN precluded any further consideration of the non-brominated nitriles.

CHEMICAL FAMILY DOWN-SELECTION REVIEW AND CONSIDERATIONS

The search for replacements for halon 1301 has been broad based with commercial sources offering several fluorocarbon products from different chemical families. Some efforts focused on finding high fire suppression efficiency agent while others sought replacement compounds that were free of any of the generally recognized disqualifying properties. The general list of desired properties includes a boiling point requirement:

> Boiling point sufficiently high that a suppressing volume fraction of 5 % (at thermal equilibrium) exists at -40 °C, the minimal design temperature for aircraft suppression system performance. This boiling point is about 25 °C.

Boiling point maxima were not rigidly applied as a general selection criteria in the compound selection and testing program. Consideration including chemical heats of vaporization, agent storage bottle temperature, nozzle design, pressurization and new technologies and methods of producing atomized or misted agent discharges were as likely to result in significantly increased volatilization and effectively a higher upper boiling point limit.

With the focus on aircraft application the limits of temperatures experienced in flight were a prime consideration and fire related agent discharge characteristics at these temperature of great interest. Dispersion testing of CF_3I at -40 °C was performed with results that were not reassuring. These tests indicated that even with its relatively low boiling point CF_3I (-22.5 °C) lacks sufficient volatilization under conditions of the testing to give assurance that a uniform extinguishment concentration would be obtained.

The potential for new agent distribution and application methods to greatly affect the performance and ultimately the usability of an agent as a fire suppressant should be kept in mind in view of the limited choices available.

CHEMICAL FAMILY OPTIONS SUMMARY

Demonstrated clearly identified chemicals and or chemical family options for application to aircraft remain unmet. No chemical studied thus far satisfactorily addresses aircraft applications demanding and unique combination of high flame suppression efficiency, low boiling point, acceptably short atmospheric lifetime, and acceptable toxicity. Should any of these constraining attributes, particularly boiling point, be relaxed it is likely that some chemical families options may well be applicable. New agent dispersion methods may facilitate use of chemicals whose boiling points are in the 25 to 35 °C range.

This extensive review and evaluation of chemical families and chemical testing has yielded a limited list of candidate chemical families that might be useable should boiling point limits be relaxed. Some of these chemical families, particularly the bromofluoroalkenes and bromofluoroethers may well include compounds with toxicity low enough to allow consideration for use in occupied areas. Chemical families such as the bromofluoronitriles, bromofluoroimines, and the n-brominated amines and imines should include relatively low boiling compounds whose applictions will likely be restricted to unoccupied areas. Additional study and testing might also allow inclusion of selected fluoroalkyl phosphorus compounds in this listing however at this point no such justification exists.

TABLE 11. CHEMICAL FAMILIES ASSESSMENT SUMMARY

Chemical Family (Example)	Overall Candidacy Assessment - Conclusions/Recommendations
Brominated fluoro alkenes (CH_2=CBr-CF_3)	Many brominated fluoro- ethenes, propenes, butenes and some pentenes of which program allowed study of only a few examples. Effective fire suppression performance, acceptable acute inhalation toxicity in some cases, and demonstrated short atmospheric lifetimes. Inability to easily screen for cardiac sensitization a major hurdle to progress. Boiling points are generally higher than 25 °C for the bromo fluoro propenes. Bromo-tetrafluoroalkenes may have the best mix of toxicity, flame suppression, and boiling point.
Brominated fluoro ethers CF_2Br-O-CF_2H	Demonstrated fire suppression effectiveness, lower boiling points, possible shorter atmospheric lifetimes if sufficient hydrogen's in structure. Toxicity may in some cases to be acceptable for some applications. Synthetic pathways converting fluoromethyl ethers to their brominated congeners provide ready approaches to other members of this family.

Bromofluoroamines may eventually offer significant promise if sources of these compounds can be located. The toxicity of this class of compounds is expected to be low and there are numerous compounds that in theory might well be considered if available. Compounds such as $N(CFH_2)_2(CF_2Br)$ could provide short atmospheric lifetimes and chemical suppression. The primary barrier to progress remains compound availability.

References

1 "Laboratory Through Full Scale: The U. S. Navy Halon Total Flooding Replacement Program," Ronald S. Sheinson, Chapter 16 in Halon Replacements: Technology and Science, ACS Symposium Series 611, Miziolek, A. W., and Tsang, W., Eds., American Chemical Society, Washington, DC, 1995, ISBN 0-8412-3327-6, pp. 175-188.

2 Sheinson, R.S., Hahn, J.E., Geary, K., and Williams, F.W., "Quantification of Physical Fire Suppression of Heptane Pool Fires," Proceedings of the Chemical land Physical Processes in Combustion Symposium, Eastern Section Combustion Institute, East Hartford, CN, 10-11 November 1977.

3 Sheinson, R.S., Gellene, G.J., Williams, F.W. and Hahn, J.E., "Quantification of Fire Suppressant Action on Liquid Pool Fires," Proceedings of the Eastern States Combustion Institute, Miami Beach, FL, 29 November - 1 December 1978.

4 R.S. Sheinson, J.E. Penner-Hahn (University of Michigan) and D. Indritz (Exxon R&D Engr Co.), "The Physical and Chemical Action of Fire Suppressants," Fire Safety Journal 15, 437 (1989).

5 Sheinson, R.S., Carhart, H.W., Musick, J.K., and Williams, F.W., "Halon Acid Production from Full Scale CR3Br Pool Fire Suppression Tests," Proceedings of the Eastern States Combustion Institute, Atlanta, Georgia, 7-9 November 1979.

---

6 Sheinson, R.S., J.K. Musick, and H.W. Carhart, "HF and HBr Production from Full Scale CF3Br (Halon 1301) Fire Suppression Tests)," J. Fire & Flammability, 12, 229 (1981).

7 Skaggs, S. R., and Nimitz, J. S., “Estimating Tropospheric Lifetimes and Ozone-Depletion Potentials of One- and Two-Carbon Hydrofluorocarbons and Hydrochlorofluorocarbons,” Environmental Science and Technology, Vol. 26, pp. 739-744, 1992.

8 Lifke, J. L., Moore, T. A., and Tapscott, R. E., *Advanced Streaming Agent Development, Volume V: Laboratory-Scale Streaming Tests*, Wright Laboratory (WL/FIVCF) and Applied Research Associates, Inc., Tyndall Air Force Base, Florida, June 1996. NMERI 96/2/32540,Vol. 5 of 5.

9 Ted A. Moore, T.A., Dierdorf, D.S., Skaggs, S.R., and Tapscott, R.E., Materials Compatibility and Agent Operational Validation for Halon 1301 Replacement: Phase IV (Volume 2 of 2), NMERI S.S. 2.32(4), March 1993.

10 Tapscott, R. E., Heinonen, E. W., and Brabson, G. D., *Advanced Agent Identification and Preliminary Assessment*, Wright Laboratory (WL/FIVCF), Tyndall Air Force Base, Florida, April 1996. NMERI 95/15/31883.

11 Floden, J. R., and Tapscott, R. E., “The Quest for Chemical Alternatives to Halon 1211,” The Military Engineer, Vol. 82, No. 537, pp. 13-15, August 1990.

12 “Denmark to Propose Phaseout for HFCs,” Ozone Depletion Today, 7 November 1996.

13 Pitts, W.M., Nyden, M.R., Gann, R.G., Mallard, G.W., Tsang, W., “Construction of an Exploratory List of Chemicals to Initiate the Search for Halon Alternatives,” National Institute of Standards and Technology, NIST Technical Note 1279, August 1990.

14 Bausum, H. T.,QSAR Estimates of Toxicity of Candidate Halon Replacement Compounds, Health Effects Program, US Army Center for Health Promotion and Preventive Medicine, 10 January, 1997.

15 DEREK is the copyright of the President and Fellows of Harvard College and LHASA UK Ltd. (1990-1995).

16 Finch, G.L., Barr, E., Nikula, K., Krone, J., Mather, J.D., “Acute Inhalation Toxicity of Candidate Halon Replacement Compounds in Rats,” Lovelace Respiratory Research Institute, Final Report April 22, 1999.

17 Gladnick, N.L., “AAWG #873, AAWG #903, and AAWG #1116: Bacterial Reverse Mutation Test in Salmonella typhimurium and Escherichia coli,” DuPont Pharmaceuticals Company, February 29, 2000.

18 Curry, P.T., “AAWG #873: In vitro Chromosome Aberration Test in Human Peripheral Blood Lymphocytes,” DuPont Pharmaceuticals Company - Stine-Haskell Research Center, November 20, 2000.

19 Horrell, P.J., “Agent 873, An Inhalation Study to Investigate the Cardiac Sensitization Potential in the Beagle Dog,” Huntingdon Life Sciences Limited, Final Report - September 16, 2002.

20 AAWG Minutes reporting results of cardiac sensitization testing of 1-bromo-3,3,3-trifluoropropene.

21 Tapscott, R.E., Sheinson, R.S., Babushok, V., Nyden, M.R., Gann, R.G., "Alternative Fire Suppressant Chemicals: A Research Review with Recommendations," NIST Technical Note 1443, National institute of Standards and Technology, Gaithersburg MD, December 2001.

22. Heinonen, E. W., Lifke, J. L., and Tapscott, R. E., Advanced Streaming Agent Development, Volume IV: Tropodegradable Halocarbons, Vol. 4 of 5, NMERI 96/4/32540, Wright Laboratories (WL/FIVCF) and Applied Research Associates, Inc., Tyndall Air Force Base, Florida, May 1996.

23. Sax, N. I., and Lewis, R. J., Sr., Dangerous Properties of Industrial Materials, Vol. 1-3, Seventh Edition, Van Nostrand Reinhold, New York, 1989.

24. Registry of Toxic Effects of Chemical Substances, Report Number DHHS (NIOSH) 87-114, Vols. 1-5, Sweet, D. V., editor, U. S. Department of Health and Human Services, National Institute for Occupational Safety and Health, Washington, DC, April 1987.

25. Junge, C. E., “Basic Considerations About Trace Constituents in the Atmosphere as Related to the Fate of Global Pollutants,” in Fate of Pollutants in the Air and Water Environments, Part I, Mechanism of Interaction Between Environments and Mathematical Modeling and the Physical Fate of Pollutants, I. H. Suffet, editor, John Wiley and Sons, New York, New York, pp. 7-25, 1977.

26 Mather, J. D., Tapscott, R E., Environmentally Acceptable Extinguishants, NGP Final Report CDS-2006-1, February 15, 2006.

27 Chattaway A., Grigg, J., Spring, D., “The Investigation of Chemically Active Candidate Halon Replacements,” Proceedings HOTWC 2003.

28 Moore, T. A., Weitz, C. A., Tapscott, R. E., An Update on NMERI Cup-Burner Test Results, HOTWC Conference Proceedings, 1996.

29 USP 5,557,010), CAS# 181951-69-9.

30 Angew. Chem. Int. Ed. Engl. 24, (1985) 161-179)

31 DesMarteu, D., O’Brien, An Efficient Synthesis of N-Bromo perhalo-1-alkanimines, J, Org. Chem., 49, 1467-1469, (1984).

32 Bauknight, C. W., DesMarteau, D., Reactions of N-Bromodifluoromethanimine, J. Org. Chem., 53, 4443-4447, (1988).

33 O’Brien, B., Thrasher, J., Bauknight, C., Robin, M., DesMarteau, D., N-Bromodifluoromethanimine, J. Am. Chem. Soc., 105, 4266-4267, (1984).