Fluoroiodocarbons as Halon 1211/1301 Replacements: An Overview

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ABSTRACT

At the 1993 NMERI Halon Technical Options Working Group Conference, a group of attendees made the decision to jointly pursue a detailed assessment of fluoroiodocarbons (FICs), particularly CF_3I, as Halon 1301 replacements. Information presented at the conference stimulated the reexamination of this family of agents, formerly abandoned as fire suppressant candidates because of a combination of the successful development of the Halons or brominated fluorocarbons (BFCs) and concerns over potential toxicity and stability problems with the FICs. **A** research plan developed by the CF_3I Ad Hoc Working Group laid out the basic criteria CF_3I would have to meet to move on to advanced development and serious consideration for fielding as a Halon 1301 replacement. The first year of testing has resulted in CF_3I having survived all the feasibility tests to-date. Other FICs such as C_3F_7I are being synthesized and tested as streaming agent replacements for Halon 1211. These chemicals will utilize the experience gained in the assessment of CF_3I to determine if they are suitable for advanced development and fielding.

INTRODUCTION

The replacement of the major Halons utilized in fire suppression and inertion has been a history of learning experiences and accompanying frustrations for technical and policy organizations responsible for replacing Ozone Depleting Chemicals (ODCs). In the case of replacing the main total flooding chemical, Halon 1301, the initial directions were to field a replacement from among chemicals currently available in so-called production quantities. This strategy resulted in industry offerings that, while safe and relatively effective, required significantly more space and constituted more weight than the Halon 1301 systems they were designed to replace. In the vast majority of cases the retrofit of Halon 1301 systems would result in costly changes to piping and other components. In the case of aircraft and other space critical applications retrofit costs were forecast to be prohibitive. In the case of Halon 1211, the chemical of choice as a streaming agent for aircraft and facility portables and 150 lb. flight line extinguishers, the Air Force development program ran headlong into a newly emerging issue, greenhouse warming, that forced the abandonment of procurement actions to field a well-tested, reasonably effective, very low toxicity alternative. The overall climate of dissatisfaction with the results of the first several years of research and the resulting alternatives, caused an eventual reconsideration of the criterion that the replacements had to emerge within a short period or time and only from production chemicals. A chemical family that had been formerly abandoned in the initial development of the BFCs as fire suppressants was the FIC group, consisting of a variety of chemicals, the simplest compound in terms of structure, being trifluoroiodomethane or CF_3I. The FICs were the sole chemical group with any realistic potential to replace the BFCs as drop-ins for a wide range of applications. It was known these iodinated compounds had the potential to be excellent fire suppressants, simply due to the presence of the iodine atom in the molecule.

Similar to bromine, iodine was hypothesized to catalytically react with free radials such as OH that sustain the fire chain reaction. However the iodine compounds were suspected to be toxic and unstable, two characteristics that, in spite of their powerful fire suppression capability, would rule them out as fire suppressants. An Ad Hoc Working Group was formed to coordinate and finance the reinvestigation of the CF_3I with particular emphasis on these issues (Table 1). In addition, materials compatibility, global environmental impacts, and manufacturing costs were part of the initial reassessment of CF_3I to insure that all the issues regarding feasibility were addressed.

Table **1** CF_3I Ad Hoc Working Group

BP Oil Exploration (Alaska), Inc.
ARCO Alaska, Inc.
Alyeska Pipeline Service Company
Boeing Aircraft Company
Pacific Scientific, Inc.
West Florida Ordinance, Inc.
American Pacific
New Mexico Engineering Research Institute (NMERI)
U.S. Coast Guard
Armstrong and Wright Laboratories, U.S. Air Force
TACOM/TARDEC, **U.S.** Army
Naval Research Laboratory, U.S. Navy
Ministry of Defence, United Kingdom

CF_3I PROPERTIES AND TESTING

CF_3I behaves almost identically to Halon 1301 in fire suppression and explosion inertion and possesses other characteristics that make it a potential drop-in replacement for Halon 1301 (Table 2). It is a dense gas with a boiling point somewhat higher than Halon 1301. This higher boiling point may restrict its use in some applications, such as military aircraft fuel tank inertion where the chemical must remain gaseous. It also provides advantages in other uses where its higher boiling point might prove useful. The same extinguishing quantity of CF_3I will weigh approximately 14% more but will occupy **8%** less volume than Halon 1301. Consequently in space critical applications CF_3I is an excellent potential replacement.

Table 2 Basic properties of CF_3I compared to Halon 1301

Property	Halon 1301	CF_3I
Boiling Point, °C	-57.8	-22.5
Liquid Density, g/ml	1.58 @ 20°C	2.064 @ 25°C
Molecular Weight, g/mole	148.91	195.91
Extinguishing Concentration, v/v%	2.9	3.1
Inertion Concentration, v/v%	6.2	*6.5*
Weight Ratio	1.0	1.14
Volume Ratio	1.0	0.92

A summary of CF_3I testing progress to the present time is contained in Table **3**

Table 3 Testing progress for CF_3I, Phase I Feasibility Testing

Test	Result	Agency
1. Cup Burner Extinguishment	Verified as 3.1 v/v %	NMERI
2. Inertion Concentration	Verified as 6.5 v/v%	NMERI
3. Ozone Depletion Potential	Estimated at 0.009	NOAA
4. Atmospheric Lifetime	Estimated at 1.15 days	NOAA
5. Toxicity Range Testing	Rats survived 15 min, nose only, 12.7%	NMERI
6. LC_{50}	15-minute, 27.4%	NMERI
7. Cardiotoxicity	Ongoing	AL/OET
8. Storage Stability/Compatibility	No breakdown, ASTM tests, 90 days	NMERI
9. Manufacturability	Ultimate price < $20/lb, 1 M lb quantity	

Toxicity

Toxicity testing of CF_3I initially consisted of limit or range testing to roughly assess its acute toxicity or lethality to determine if it were reasonably safe for total flood applications. Range testing of rats for a 15 minute, nose only exposure to CF_3I at 12.7% or approximately four times the extinguishing concentration, demonstrated that it would be reasonably safe for total flood applications. The 15 minute LC50 was recently determined to be 27.4%. Current testing is determining the cardiotoxicity of the compound in a standard test using epinephrine challenged dogs.

Acute toxicity evaluations of CF_3I showed no evidence of CF_3I induced abnormal clinical findings for thyroxine (T4, thyroid function), hematology, and clinical chemistry and clinical pathology. Gas uptake kinetics comparing CF_3I and Halon 1301 showed that both had relatively poor solubility in blood and that both were slowly metabolized, if at all.

The carcinogenic potentials of Halon 1301 and CF_3I were evaluated using a Quantitative Structure Activity Relationship (QSAR) approach. Using a limited data base, the carcinogenic potential of CF_3I was estimated to be no greater than that of Halon 1301. A great deal of further studies and work in this area is needed and planned in order to better quantify this potential.

At this point in time no toxicological evidence has been found that would preclude continued efforts to assess CF_3I as a Halon 1301 replacement.

Stability

The stability testing of CF_3I was conducted at NIST and NMERI using entirely different sets of conditions. The NMERI test protocol was based on ASTM Standards and also incorporated materials compatibility tests. The test matrix is shown in Table 4. The test procedure consisted of a weekly FTIR analysis of the volatilized liquid phase of the chemical, with specific focus on determining the HF, CO_2, CO and C_2F_6 content. Within the detection limits of the equipment utilized in the experiments, no breakdown of the agent was detected at the most recent analysis interval, 90 days. During the testing one accidental excursion of short duration to 240°F produced strong HF peaks of about 100 ppm in the sample containing water vapor. The testing will continue for a total of 180 days. The NIST testing, conducted as part of the Air Force aircraft engine nacelle and dry bay Halon replacement program, detected evidence of decomposition at around 300°F. Analysis of the data indicates that CF_3I appears to undergo degradation between 170°F and 300°F. As with other issues regarding the FICs, comparable data for Halon 1301 is unavailable and it is therefore difficult if not impossible to determine on a relative basis the behavior of FICs relative to BFCs. For nominal long term storage conditions it would appear that there is not a problem with CF_3I stability. For severe operating conditions such as would be encountered in the vicinity of a fighter aircraft APU, temperatures could exceed 350°F for short periods of time. CF_3I may not prove to be adequate for these applications. Again it should be noted that the behavior of Halon 1301 under this type of severe scenario is largely unknown.

Table 4 Test Matrix for CF_3I Stability Testing		
Sample	**80°F**	**170°F**
CF_3I neat	X	X
+ N_2 300 psi	X	X
+ N_2 300 psi + 0.5% water	X	X
+ N_2 600 psi	X	X
+ Air 300 psi	X	X

The stability test data for CF_3I to-date is encouraging in that it indicates that for a wide variety of storage conditions the agent will be stable. Future efforts will attempt to clearly define the stability parameters and conditions for onset of instability as a function of temperature and pressure. The effects of water vapor in varying concentrations and its effects on stability will also be investigated.

Materials Compatibility

The corrosion behavior of a range of materials that are likely to be exposed to CF_3I in total flood applications was explored in parallel with the stability testing. Stainless steel (21-6-9 Stainless or Nitronic 40), 7075 Aluminum, casting brass, and elastomers (Buna N, EPDM, and neoprene) were exposed under a variety of temperatures and pressures. The results of this testing at the most recent or 90 day interval were examined for their results. The outcome of this testing is shown in Tables 5 and 6.

Table 5 CF_3I metals corrosion testing, intermediate results at 90 days		
Material	**Range of Weight Change, g**	**Range of Corrosion Rates, mmlyr**
Stainless steel	0.0000 to 0.0006	-0.0006 to 0.0002
Carbon steel	0.0002 to 0.0188	0.0010 to 0.0098
Brass	0.0004 to 0.005 I	-0.0001 to 0.0040
Aluminum	0.0004 to 0.0019	-0.0001 to 0.0027

Table 6 Summary of intermediate CF_3I elastomer compatibility testing at 90 days			
	<------Immediate Changes------>		
Material	% Volume Change	% Weight Change	% Hardness Change
Buna N	-1.1 to27.3	28.4 to 72.5	-12.3 to 17.0
EPDM	-28.4 to -15.0	-25.8 to 8.6	16.2 to 33.8
Neoprene	-10.6 to 28.5	15.4 to 66.6	-20.1 to 27.0
	<------24 Hour Changes------>		
Material	% Volume Change	% Weight Change	% Hardness Change
Buna N	-22.4 to -15.4	-12.4 to -9.5	38.0 to 55.6
EPDM	-28.7 to -16.0	-28.0 to -23.1	37.1 to 38.6
Neoprene	-23.8 to -15.6	-17.0 to -4.0	19.6 to43.4

The brass samples maintained at 170°F had pink discoloration while the **90** day, 80°F carbon steel samples were covered with black oxide coating, the suspicion being that the agent had some amount of HF contamination. In summary the materials compatibility testing demonstrated no degradation was detected at 80°F and 170°F under a variety of conditions. An accidental transient to 240°F and testing at higher temperatures indicates that thermal instability can occur above 200°F. Corrosion rates for CF_3I are minimal for all metals exposed in the feasibility testing.

Manufacturers

There are two declared U.S. manufacturers of CF_3I and other members of the fluoroiodocarbon family: Pacific Scientific and West Florida Ordinance. Pacific Scientific is in the process of increasing production from 50 to 500 Ib. per day and is building a new plant in Oklahoma that will have an ultimate 3-5 million lb/yr capacity. West Florida Ordinance has a capacity of 100 Ib. of fluoroiodocarbon capacity per **8** hour shift and, depending on demand, could operate multiple production shifts. They are in the process of constructing a new plant in Tennessee that could manufacture a variety of fluoroiodocarbons. Pacific Scientific is marketing CF_3I under the trade name Triodide$_{tm}$ while West Florida Ordinance is using the trade name Iodoguard$_{tm}$. There are also several producers of laboratory quantities of these chemicals **as** well as off-shore production in locations such as Russia and Japan.

SNAP Approval

In order to be able to use the fluoroiodocarbons **as** Halon **1211**/1301 replacements within the U.S. the Environmental Protection Agency (EPA) must approve the substitution and formally list the replacement chemical as part of a legislated program called SNAP: Significant New Alternatives Program. In order for this to occur the chemical must have been extensively tested for its intended use and for its toxicology. For unoccupied space use the LC_{50} of the chemical must be known and must be greater than its fire extinguishing concentration. If the chemical is intended for use in occupied spaces or normally occupied spaces, the cardiotoxicity of the agent must be determined and must be greater than its fire extinguishing concentration. Developmental and subchronic toxicology is also required for agents prior to widespread use. For this latter case the 90 day inhalation test at the design concentration for fire suppression is the test normally conducted. The design concentration is usually stated at about the cup burner fire extinguishing concentration plus 20% to account for distribution anomalies. The cup burner value for CF_3I is about 3.1% and the design concentration would be about 3.7%. The SNAP submittal to EPA for CF_3I is currently being assembled by Pacific Scientific and will be made in stages. First, approval will be requested for unoccupied space use when the LC_{50} results are known. Second, approval for use in occupied spaces will be requested when the cardiotoxicity results are available.

Global Environmental Impacts

CF_3I and other FICs have a strong tendency to photolytically decay in the visible light spectrum, resulting in a very short atmospheric lifetime, estimated as 1.15 days. The atmospheric lifetime for releases at higher altitudes is thought to be significantly shorter. The ODP for CF_3I has been initially estimated to be about 0.009, based on an assumption that 5% of all discharges are transported directly to the stratosphere in a matter of hours. Future work entails the determination of the kinetics of several as yet unknown reactions such as the fate of IO, BrO, and several other decomposition products. Use aboard aircraft could be somewhat dependent on the results of an effort to gather data on actual aircraft Halon 1301 discharges versus altitude in order to determine if there is reason for concern about these releases.

Future Development Work

The program to assess CF_3I's capabilities and limitations has advanced rapidly in the past 9 months. An interim meeting of the Working Group to assess progress and future requirements was held in mid-March 1994 at NMERI. The Group concluded that research and development efforts were progressing satisfactorily and that in some areas further research would be required to provide a complete picture of CF_3I characteristics. The major areas of concern at this juncture are the hot surface (pyrolysis) products of CF_3I, its thermal operating envelope, the effects of water vapor and other impurities in storage, and its subchronic and developmental toxicity. Additionally it was determined that medium scale testing should be initiated and that NRL's 2000 ft^3 chamber would be the appropriate test bed for determining the distribution, stratification, and other parameters needed to progress to full scale testing. Future full scale testing will be applications dependent, with the Navy, Coast Guard, and Air Force having a variety of scenarios slated for testing.

FLUOROIODOCARBON STREAMING AGENTS

The feasibility analysis method used by the CF_3I Ad Hoc Working Group will be adopted as appropriate to sort through several of the large single iodine molecules to determine if there are suitable Halon 1211 replacements from among these higher boiling point compounds. Table **7** shows the compounds that are **or** will be considered and basic **known** data about them.

Table 7 Properties of proposed Halon 1211 replacement fluoroiodocarbons

Property	H1211	C_2F_5I	C_3F_7I	C_4F_9I	C_4F_8I
BP, ^{o}C	-4	12	41	67	*85*
Atm Life	10 yrs	<2 days	<2 days	<2 days	<2 days
ODP	*2.12*	-0	~0	~0	-O
Ext Conc	3.2%	2.1%	3.0%	2.8	3.0
LC_{50}, %	12	>1	>3	unk	unk

At the present time a 10 Ib. quantity of recently synthesized C_3F_7I is being utilized for Feasibility Testing as was accomplished with CF_3I. Fire suppression effectiveness, and toxicity range testing are underway and the results of these efforts will be available shortly. The next set tests will consist of materials compatibility and stability ASTM assessment and LC_{50} determination. Small to medium scale testing will also be conducted in side-by-side testing with **known** agents to determine its relative performance.

CONCLUSIONS

The testing **of** FICs was initiated almost one year ago and has thusfar demonstrated that CF_3I has meets all the criteria established for an environmentally and occupationally safe drop-in replacement for Halon 1301. Intermediate test results at 90 days of a 180 day stability test cycle indicate that the material appears stable. Toxicity testing indicates that it more acutely toxic than Halon 1301 but still within acceptable limits **for** its intended purposes. These **two** issues, stability and toxicity are the major questions about CF3I and their successful resolution is essential for fielding this chemical. Global environmental studies show it to have a short atmospheric lifetime of 1.15 days and an ODP of 0.011 based on a conservative model. Further analysis is ongoing and if the ODP is found to be below the current estimate it will mean that CF_3I is acceptable in terms of its global environmental impacts. Additional work on determining aircraft releases versus altitude will affect aircraft applications **of** CF_3I. Phase 2 testing has been initiated to determine its exact LC_{50}, accomplish subchronic and developmental toxicity testing, and establish the stability envelope for applications, both thermally and in the presence of water vapor and other common contaminants. An ASTM standards group has been formed and a CF_3I standard for purity will be created. An NFPA standards committee is being formed to initiate the writing of a standard for total flood applications of CF_3I. At least two manufacturers have invested in plants to create sufficient capacity to fulfill all foreseeable requirements. Active competition is already occurring and the price of CF_3I has been reduced from over $500 per pound to around $100 per pound at present. Ultimate price predictions vary widely, from a low of $10 to about $25 per pound for several million pound annual production quantities. CF_3I also is under active consideration as a refrigerant and foam blowing agent and if it finds wide applications additional capacity may be required.

References

The material in this paper is largely the result of CF3I Ad Hoc Working Group meetings. Formal reports on much of the work described above will be published in the coming months Some of the toxicological work to-date is available from the Toxic Hazards Division of Armstrong Laboratory, U.S. Air Force, Wright Patterson Air Force Base, Ohio.