The USAF Halon Replacement Program –
Historical Perspective and Current Status

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Introduction

The search for Halon alternatives has been elusive. As potential replacements have come to light, new regulations have come to play making it difficult to come up with a true drop-in replacement. The USAF has taken a leadership role in performing research in developing new alternatives. Under DOD's Project Reliance, the USAF has been designated lead service for the development of Halon 1211, and its work on engine nacelles, and dry bays has provided great contributions in the development of Halon 1301 replacements. The USAF has continuously pushed the envelope on the development of new chemical substitutes. Its role has been in chemical synthesis and mechanistic innovation rather than to serve as a tester and evaluator of commercially available solutions.

The USAF team of researchers includes partners in academia, of which the University of New Mexico, the University of Florida, and the University of Massachusetts have played leading roles. Partnerships with other services has been through participation in working groups, such as the Advanced Agent Working Group, and, more recently, through the DOD-sponsored Next Generation Program. Due to the pressing ozone-depletion problem and the sense of urgency imparted on the DOD by Presidential Directive and supported by the Montreal Protocol and its amendments, close coordination and cooperation with the USEPA has been a cardinal element of the USAF approach.

In this paper, we present a chronological and historical overview of the various successful paths taken by the USAF to identify and develop halon alternatives, and the current status of the replacement work both for Halon 1211 and for Halon 1301.

1985-1986
Laying the Foundation

Vienna Convention: On 22 March 1985, with entry into force on 22 September 1988, the Vienna Convention for the Protection of the Ozone Layer was agreed upon. The Vienna Convention called for an investigation of impacts to ozone layer and impacts of ozone layer depletion, and recognized that fully halogenated bromoalkanes deplete stratospheric ozone.

In anticipation of possible restrictions on halon availability and to investigate the potential for improved agents, in August 1985, the U.S. Air Force initiated a project in cooperation with the U.S. Navy on “Next Generation Fire Extinguishing Agents.” This project became a major part of the Air Force Ozone Impact Mitigation Program. Several initial decisions were made.

1. To accelerate development and to avoid unnecessary work, a parallel, rather than serial path, would be followed. Upon identification of a promising replacement, less promising routes would be abandoned, at least temporarily, to focus on such materials.

2. To avoid the delays inherent in editing and publishing formal reports, papers, briefings, and forums would be extensively utilized to get information into the hands of the fire protection research and user communities as soon as possible.

3. The impact on stratospheric ozone is of prime consideration in criteria for a next-generation fire extinguishant and is a driving force for agent development.

4. The project was an important part of the Air Force Ozone Impact Mitigation Program designed to respond rapidly as regulatory actions were defined [1].

These decisions have been employed throughout the Air Force halon replacement program. In particular, items 3 and 4, have resulted in a number of changes in direction.

In the very early part of the program and before the potential severity of regulations on ozone depleting chemicals was well defined, chlorofluorocarbons (CFCs) were examined as short-term halon replacements. It is interesting that actual field-testing indicated that CFCs were among the best of the non-brominated halocarbons in fire suppression. As the potential for restrictions on CFCs became more obvious, these chemicals were dropped from consideration. During this program also, a large number of tools for examining fire suppression were developed. Perhaps the most important were a uniquely designed cup burner for testing of small amounts of material for R&D and what is now known as the Chemical Options Database for tracking properties of potential replacements [2].

1987-1989
HBFCs and HCFCs

Montreal Protocol: On 16 September 1987 the Montreal Protocol on Substances that Deplete the Ozone Layer was signed and it entered into force on 1 January 1989. As first written, the Protocol required a 50% reduction in CFC-11, 12, 112, 114, and 115 by 30 June 1999, and a cap on the production of Halons 1301, 1211, and 2402.

As a result of the work done under the program on “Next Generation Fire Extinguishing Agents,” it became obvious that halocarbons were of particular interest as halon substitutes. As a result, in December 1988, a new Air Force program, “Halocarbons as Halon Replacements,” specifically targeting these compounds was initiated. However, the Montreal Protocol showed that regulations were going to be sufficiently severe that no completely halogenated saturated hydrocarbons containing bromine or chlorine could be considered as halon replacements. Accordingly, a programmatic change was made to emphasize hydrogen-containing halocarbons [3], and, in 1989, hydrobromofluorocarbons (HBFCs), hydrochlorofluorocarbons (HCFCs), and perfluorocarbons were announced as potential halon replacements [4]. Later that year, as a result of the Air Force initiative, the specific agents HBFC-22B1, HCFC-22, HCFC-123, HCFC-124, and blends of these materials were publicly reported as candidates [5]. The specific compounds mentioned above or blends containing these materials have now been commercialized, although HBFC-22B1 was commercialized only briefly.

1990-1991
PFCs, HFCs

London Amendment: On 29 June 1990, the London Amendment to the Montreal Protocol was signed and entered into force on 10 August 1992. This amendment required the phase-out of CFC production (in industrialized nations) by the year 2000; a 50% reduction in halon production by 1995 with a 100% reduction by 2000; and phase-out of HCFC production by 2040 or earlier if possible).

At this time two Air Force sponsored reports were published by NIST [6, 7]. These reports, one on a list of chemical compounds for investigation and the other on screening methods and criteria, helped lay the foundation for future research directions.

Due to concern that HCFCs would be severely restricted, research started prior to the London Amendment to find non-HCFC agents, although significant work had been done on the HCFCs. Of particular interest were perfluorocarbons (PFCs or FCs) and hydrofluorocarbons (HFCs). As early as October 1989, HFCs, including HFC-23 and HFC-125, and PFCs, including FC-218 (perfluoropropane) had been reported as being considered under the Air Force program [5, 8], and in July 1990, FC-218 was announced as a candidate agent [9]. On 5 October 1990, patent applications acknowledging support and rights of the U.S. government were filed (and, patents were eventually issued) on HCFC-123, HCFC-124, HFC-125, and FC-218 [10, 11].

In September 1990, the U.S. EPA initiated a project to look specifically at PFCs as total flooding agents, and in July 1991, the North Slope Oil and Gas Producers initiated sponsorship of a program on PFCs, with specific emphasis on agents for North Slope petroleum fire protection. As a result of these and Air Force efforts on perfluorocarbons, in September 1991, perfluorohexane (FC-5-1-14) was announced as a promising candidate for streaming [12]; and in December 1991, perfluorobutane (FC-3-1-10) and other perfluorocarbons were announced as candidates for halon replacement [13].

Looking down the line, it was evident that global warming would eventually, become an important issue, and that this could impact the use of perfluorocarbons as halon replacements. There was, therefore, increasing interest in HFCs as halon replacements. HFC-125 and other

HFCs had already been identified as halon replacements in Air Force work [10, 11], and work sponsored by the U.S. EPA had identified HFC-227ea and HFC-236fa as candidates and had recommended them for laboratory testing [14].

1992-1996
Iodides, Advanced Agents

Copenhagen Amendment: On 25 November 1992, with an entry into force on 14 June 1994, the Copenhagen Amendment to the Montreal Protocol was signed. The amendment called for the phase-out of CFCs by 1996; the phase-out of halons by 1995, a 99.5% reduction in HCFCs by 2020; and a phase-out of HBFCs by 1996. The Air Force had ended work on HBFCs relatively early in view of the evidence that these compounds would have unacceptable ozone depletion potentials, and this decision was justified in view of the Copenhagen Amendment.

As a result of tightening restrictions on ozone depleting materials, work had started relatively early on new families of compounds. As early as November 1990, iodocarbons were announced as potential candidates [15], and in December 1991, trifluoromethyl iodide (CF_3I) was announced as a specific candidate agent [16]. As a result of an initiative sponsored by the CF_3I Working Group (which included Air Force, Army, Navy, North Slope Oil and Gas Producers, and other participants and was established in May 1993), CF_3I was eventually commercialized as a halon replacement.

Moreover, work under the Advanced Agent Working Group, with Air Force, Army, Navy, and commercial participation, identified a number families of non-halocarbon agents as potential halon replacements [17], and the results of this initial study have led to several initiatives under both Air Force and Next Generation Fire Suppression Technology programs.

1997-
Tropodegradable Halocarbons

Kyoto Protocol: On 11 December 1997, in Kyoto, Japan, delegates from 160 nations agreed to adopt the Kyoto Protocol to the United Nations Framework Convention on Climate Change, a treaty that requires industrialized countries to cut their emissions of greenhouse gases by an average of 5.2 percent below 1990 levels in the years 2008-2012. Individual reduction targets vary; the U.S. target is 7 percent. The United States and the other parties have until March 1999 to ratify the protocol.

The potential impact from global warming concerns was recognized early. In fact, bromocarbons with low atmospheric lifetimes (now termed “tropodegradable” halocarbons) were announced as potential candidates in the spring of 1991 [18]. These compounds have received increased importance with the signing of Kyoto Protocol. Work on tropodegradable compounds, with an emphasis on unsaturated bromocarbons, is continuing under U.S. Air Force sponsorship (Halon 1211 replacements), Next Generation Fire Suppression Technology Program sponsorship (primarily, Halon 1301 replacements), and the Advanced Agent Working Group (explosion inertion a major focus). USAF work has also shown that bromoalkane blends are very promising for Halon 1211 replacement. These materials also appear applicable to total-flood fire protection. Like other tropodegradable compounds, higher molecular weight bromoalkanes should have acceptable lifetimes and global warming potentials.

Current Status: Halon 1211

The USAF approach to finding 1211 replacements has used the latest and state of the art techniques in quantitative chemometrics. The program has successfully relied on Quantitative Structure-Property Relations algorithms which make use of the relationship between relevant structures such as molecular topology, molecular connectivity, bromination, and the sought property such as fire extinguishing concentration, toxicity, atmospheric lifetime, ozone depletion potential, global warming potential, boiling point, and vapor pressure. This method allowed for the selection of single constituent compounds that, in principle, could be used as direct replacements. A second approach of using blends of known chemicals with desirable properties is a parallel approach, which has yielded a very promising replacement.

A database of over 1000 compounds, whose structures can be calculated, was matched with a database of properties associated with these compounds. The resulting matrix allowed for the prediction of structures based on desired properties by a robust method of extrapolation fitting.

After considerable search it was found that our choice of single compounds was reduced to the following compounds:

1-bromo-3,3,3-trifluoropropene
2-bromo-3,3,3-trifluoropropene
3-bromo-3,3-difluoropropene
4-bromo-3,3,4,4-tetrafluorobutene
2-bromo-3,3,4,4,4-pentafluorobutene
2-bromo-3,4,4,4-tetrafluoro-3-trifluoromethoxy-1-butene

Current Status: Halon 1301 for Normally Unoccupied Spaces

A US EPA analysis of data suggesting an exposure limit of 150 ppm as protective for occupational usage, as well as new advances in cardiotoxicological assessment, has led the USAF to reconsider the use of CF3I for normally unoccupied spaces such as engine nacelles, APU's, and dry bays. The EPA draft risk screen indicates that endpoints such as chronic toxicity resulting from CF3I exposure are mitigated when the exposure levels are kept below 150 ppm on a routine basis. EPA is evaluating the use of CF3I in a number of different end uses including consumer refrigeration applications.

Cardiac toxicity of CF_3I is also a concern. However, new toxicological evaluation tools developed at AFRL, give us a better insight into toxicological risk. The technique known as Physiologically-based Pharmaco-Kinetic (PBPK) model allows for the correlation of exposure time and level to blood concentration. This technique would then allow for a meaningful interpretation of exposure scenarios and their likely consequences based on a verifiable parameter, namely blood concentration. For example, this technique would be able to verify that an exposure at the LOAEL value for 5 minutes can cause a totally different response than an exposure at the LOAEL value for 10 seconds. These scenarios are then valuable and used in determining a required risk assessment for new substances.

These aspects have caused the USAF, and the DOD community in general to take a second look at CF_3I as a total flooding agent for normally unoccupied spaces in weapon systems such as engine nacelles, APU's, and dry bays for the F-15, F-22, C-130, C-17, JSF, and fuel ullage inertion for the F-16.

Current work concentrates on resolving outstanding technical issues such as cold discharge performance, gaseous phase materials compatibility, and further work on toxicological characterization of CF_3I. These studies are being funded by the Next Generation Program (DOD) and internal USAF R&D funds.

Summary

The USAF work to find suitable replacements has been highly successful and yielded a number of solutions. Current impetus on global warming and tropospheric lifetime has centered attention now on tropodegradable compounds as suitable replacements. New data on chronic toxicity has caused renewed interest in the USAF to look at CF_3I as a suitable drop-in replacement for normally unoccupied areas.

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