HALON REPLACEMENT RESEARCH - A HISTORICAL REVIEW OF TECHNICAL PROGRESS AND REGULATORY DECISION POINTS

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> "...and it will fall out as in a complication of diseases, that by applying a remedy to one sore, you will provoke another; and that which removes the one ill symptom produces others...," Sir Thomas More, *Utopia,* 1516.

INTRODUCTION

In 1985, under the lead of the U.S. Air Force (USAF), and with the U.S. Navy as a co-sponsor, research was initiated on chemical replacements for halon fire and explosion protection agents. Under Project Reliance, a tri-service agreement to assign ''leads'' to different services to avoid overlap in R&D, the Air Force is now designated the lead military organization in development of Halon 1211 replacements. However, in the early days of halon replacement work, the Air Force was involved in halon replacement research in general. This work, which emphasizes chemical substitutes for halons rather than just testing and certification of commercial industry announced solutions, has continued not only under USAF leadership, but in work sponsored by the U.S. Environmental Protection Agency, Advanced Agent Working Group (AAWG), CF_3I Working Group, U.S. Army, U.S. Navy, and North Slope Oil and Gas Producers. Some chemical manufacturers have also participated in the working groups. More recently, the Next Generation Fire Suppression Technology Program (NGP) has become a major contributor in the quest for halon substitutes. These have been the only non-industry-directed initiatives in the United States to have resulted in commercialized halocarbon replacements for halons and were first to result in announcing hydrobromofluorocarbon (HBFC), hydrochlorofluorocarbon (HCFC), perfluorocarbon (PFC), and fluoroiodocarbon (FIC) halon replacement candidates. Although non-industry initiatives are emphasized here, industry has been heavily involved in research and development and has made important investments in the work needed for final commercialization.

In this paper, we present an historical overview of these, on the whole, highly successful efforts to find and identify halon replacements. The paper also discusses how increasing regulatory pressures have required changes in rationalization and direction of the various research programs, each of which resulted in identification of a new family of chemicals. For the most part, this overview is on the development of new chemical agents rather than post-development testing. Moreover, the emphasis is on halocarbons, which are the primary chemicals to be commercialized to date. Thus, no attempt has been made to present the excellent work done by organizations such as the National Institute of Standards and Technology (NIST) and the Air

Force on agent testing for aircraft engine nacelles, the Navy and **US** Coast Guard on evaluation of total flooding agents for shipboard use, and the US Army on evaluation of agents for tracked vehicles. Nor has any attempt been made to give an overview of work done by agent and hardware manufacturers, whose initiatives often have focused on testing and evaluation or involve inhouse, proprietary agent research. Moreover, the work reviewed here does not include new technologies such as gas generators and misting systems. Because **Air** Force initiatives have formed a common thread throughout much of this work, Air Force work is emphasized. Owing to the very large number of references, only citations essential to specific statements have been given. In particular, no attempt has been made to reference the numerous reports that have resulted from this work.

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 **US** Air Force initiated a project in cooperation with the **US** 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 (CFC) were examined as short-term halon replacements. It is interesting that actual field testing indicated that CFCs were among the best of the nonbrominated 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 known as the CGET Chemical Options Database (formerly the Halocarbon Database [2]) for tracking properties of potential replacements.

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 (HBFC), hydrochlorofluorocarbons (HCFC), 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 AND 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 phaseout 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 phaseout 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 (PFC or FC) and hydrofluorocarbons (HFC). 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 AND 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 phaseout of CFCs by 1996; the phaseout of halons by 1995, a 99.5% reduction in HCFCs by 2020; and a phaseout 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 contained 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%** below 1990 levels in the years 2008-2012. Individual reduction targets vary; the U.S. target **is** 7%. 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.

SUMMARY

The halon replacement program with the U.S. Air Force playing a lead role has been highly successful. Multilateral military, EPA, and Working Group initiatives have led the way in the identification of most halocarbon replacements for halons commercialized to date. As each new agent has been identified, however, increasing regulatory restrictions (Vienna Convention, Montreal Protocol, London Amendment, Copenhagen Amendment, Kyoto Protocol) have required changes in targets (CFCs, HCFCs, PFCs, HFCs, tropodegradable halocarbons). With the potential impact of the Kyoto Protocol, tropodegradable halon replacements with both low or zero ODPs and exceptionally low atmospheric lifetimes have now become a major focus.

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