

Advanced Agent Working Group

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For many years, Halon 1301 has been used for total-flood fire and explosion protection. However, it has been identified as a stratospheric ozone-depleting substance, and production has now been banned in industrialized nations under the Montreal Protocol, an international treaty. To date, no Halon 1301 substitute has been identified that provides total-flood protection against fires and explosions in normally occupied areas without major changes in system hardware. To address this problem, an Advanced Agent Working Group (AAWG) has been formed. The goal of the AAWG is to identify chemically active agents (CAAs) as substitutes for Halon 1301 in normally occupied areas.

BACKGROUND

On 23 August 1994, representatives of North Slope Oil Producing and Transmission Companies met with other members of the "CF₃I Working Group" at the New Mexico Engineering Research Institute (NMERI) in Albuquerque, New Mexico, USA, to discuss the results to date with CF₃I and the needs for future research. The following are the conclusions from that meeting:

1. No replacement chemical or alternative system that has an effectiveness essentially equal to that of Halon 1301 has yet been identified for total-flood use in normally occupied areas.
2. Most work to date has emphasized agent testing rather than agent identification.
3. With the exception of the CF₃I program and studies for the U.S. Air Force now under way on advanced streaming agents, most work has been on "readily available" physically active agents (PAAs) with relatively little work on advanced chemically active agents (CAAs).
4. There is a need to go back to "square one" and specifically identify and assess the potential of advanced total-flood CAA candidates, at which time a decision can be made on continuation of work toward an advanced total-flood agent.

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5. The “**CF₃I** Working Group” was remarkably successful in accomplishing what it was intended to do (**assess** and bring to commercialization **CF₃I** as a halon replacement).

6. In view of the success of the CF₃I group, an Advanced Agent Working Group (AAWG) was formed. This new group emphasizes replacement of Halon **1301** in normally occupied areas with a CAA. Both fire extinguishment and explosion protection are emphasized.

AAWG MEMBERS

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INITIAL AAWG PROJECT

To determine the probability of identifying a CAA for use in normally occupied areas, a short-term project has been initiated to answer four questions:

1. What mechanisms are available for CAAs for protection against fires and explosions?
2. **Based** on these mechanisms, what families of chemicals could provide an advanced replacement for Halon **1301**?
3. What is the preliminary assessment of manufacturability, global environmental impact, and toxicity for these families?

4. Taking all of the above into account, what are the prospects for a halon replacement for total-flood explosion and fire protection of normally inhabited areas without major hardware changes?

Once answers to these four questions are in hand, participants can make an intelligent decision about the probability of success in continued work and about those chemicals most likely to provide an answer.

Task 1: Technology Assessment

The first question to be answered is "What mechanisms are available for CAAs for protection against fires and explosions?" A survey of all information on explosion protection and fire suppression testing and on mechanisms of chemical protection agents has been performed. Much of the data needed has already been collected in efforts at NMERI and at the National Institute of Standards and Technology (NIST); however, it has not been thoroughly analyzed for development of a total-flood agent for normally occupied areas. Mechanisms of steps in combustion and, in particular, extinguishment is being emphasized.

Methodologies and software utilities have been established for computerized storage, manipulation, and retrieval of information collected during this project. Microsoft Access™ is being used for this task. This relational database allows the formation of separate, but related files, which avoid duplication of data but allow combined transfer into appropriate word processing and spreadsheet programs. Moreover, the database allows expansion to cover possible future work. Very important is that copies can be provided participating members who have Windows™ operating systems. Note that with an Access™ Distribution Kit, multiple executable copies can be legally distributed. It is not necessary to have the Access™ software on the computer.

A detailed search strategy has been developed. Mechanisms of explosion and fire inertion and suppression are of primary interest. The search includes collection and analysis of both chemical and physical mechanisms. Most information retrieval has been performed using documents already available and backtracking to earlier references or forward tracking to other papers by the same authors.

Task 2: Selection and Grouping of Chemicals and Chemical Families

The second question to be answered is "Based on these mechanisms, what families of chemicals could provide an advanced replacement for Halon 1301?" To answer this question, the data collected in Task 1 is being reviewed and chemicals or families of chemicals are being selected for further assessment in Task 3. This step is highly chemistry oriented. Much of Task 2 is being performed at the same time that data are being collected in Task 1. Moreover, as assessments of compounds and chemical families are made in Task 3, other candidate compounds or families are being identified, and the list will be revised.

Throughout Task 2, contact with other experts in the field and with the members of the AAWG is being maintained. On-going discussions and circulation of preliminary draft reports and databases are essential.

Task 3. Assessment of Potential of Chemicals and Chemical Families

The third question is "What is the preliminary assessment of manufacturability, global environmental impact, and toxicity for these families?"

Synthetic and manufacturing procedures for the chemical classes specified in Task 2 and for other chemical classes that may arise are being reviewed. This portion of the project is essential to ensure that sufficient information is available to properly **assess** the final list of chemicals. The information collected is being used to assess manufacturability or synthetic routes to chemicals needed for testing.

Literature and contacts with atmospheric scientists are being used to make preliminary assessments of Ozone Depletion Potentials (ODPs), Global Warming Potentials (GWPs), and Atmospheric Lifetimes. In some cases, estimation techniques may be used. In many cases, the potential for environmental impact will be obvious from the chemical structure.

The toxicity of agents in the chemical families identified is being estimated using whatever toxicity information is available, using toxicological indices for selected individual related compounds, and, possibly, in some cases using Quantitative Structure-Activity Relationships (QSARs). The toxicity assessment is being discussed with outside toxicology experts.

Task 4: Determine Prospects

Working with members of the **AAWG**, outside experts, and others, the likelihood of a total-flood halon replacement for normally occupied areas requiring minimal hardware changes will be determined. Current hardware configurations will be assessed, and impacts due to alternative agents evaluated with respect to costs, equipment size and weight, and reduced capabilities.

Schedule

All tasks are scheduled to be completed by 1 August 1995.

DATA STORAGE AND INTERCHANGE

One of the difficulties in investigating a large number of new compounds is how to manage the **data associated** with the compounds and how to facilitate data interchange among the participants. **The** following databases and **software** have been implemented to perform those tasks.

NMERI HALOCARBON DATABASE@

Although this project **emphasizes** non-halocarbon agents, other chemicals, primarily fluorocarbons, could be used **as** carriers to facilitate use of higher boiling point materials **as** total-**flood** agents. The existing **NMERI HALOCARBON DATABASE**^o (Reference 1) which contains physical and chemical data on nearly 900 compounds, has been updated with additional

information to allow better selection of carriers in these applications. Among these chemicals are 108 new compounds that are being considered for advanced agents. A new feature of these records is a pop-up form which displays the structure of some compounds. All values in this database are linked to references in the **NMERI LIBRARY DATABASE**.

REFERENCE I

The **ADVANCED AGENT REFERENCE DATABASE** has been developed to display references in the **NMERI LIBRARY DATABASE** that relate to advanced agents. The database provides a citation suitable for inclusion as a reference, key words, and the abstract. In addition, a separate conclusion field, into which ideas expressed by the reference can be written, and a concepts field, into which ideas on how the ideas presented by the reference could be used in fire suppression can be written, are also supplied. **As** new references are entered in the **NMERI LIBRARY DATABASE**, those which correspond to advanced agents can easily be added to the **ADVANCED AGENT REFERENCE DATABASE**. Reports have been developed for the database to present either summary data on all references or detailed information on individual references.

Advanced Agent Home Page

A Welcome Page has been established on the New Mexico Engineering Research Institute's server on the World Wide Web (WWW) to provide information of the activities of the Advanced Agent Working Group. This Home Page will allow members of the **AAWG** to exchange information via a bulletin board-type guest book. Comments can be entered which will be available to all to read. The welcome page is part of the Center for Global Environmental Technologies (CGET) welcome page, which is in turn part of the New Mexico Engineering Research Institute (NMERI) welcome page, which falls under the University of New Mexico home page. The World Wide Web address for the Advanced Agent Working Group is:

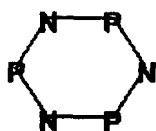
<http://nmeri.unm.edu/nmeri/cget/aawg.html>

AGENT CLASSES IDENTIFIED TO DATE

Three! promising classes of potential advanced agents identified thus far are phosphorus nitrides, silicon and siloxane compounds, and neutral-charge transition metal complexes. These are briefly discussed below. Identification of additional advanced agents is expected.

Phosphorus Nitrides

Phosphorus nitrides are now known to be highly effective flame extinguishing agents (Reference 2). These materials exist **as** two groups: cyclic compounds containing a cyclic backbone (usually containing alternating phosphorus and nitrogen atoms) and linear compounds, which have a linear chain backbone (but which also may contain cyclic substituents along the chain). The latter are often polymers whose exact structures have not been fully characterized. Examples are shown below for a six-member cyclic ring and for a four-member chain.



Cyclic



Chain

In some cases, cup burner extinguishment concentrations as low as 0.3 percent (compared with 3 percent for Halon 1301) have been found. Moreover, some of the compounds are believed to have a very low toxicity. Much work remains to be done with the phosphorus nitrides. In particular, laboratory syntheses are required to be able to evaluate the most promising materials.

Silicon Derivatives

Silicon derivatives are highly promising. It is known that many materials containing silicon-bromide and silicon-chloride bonds are highly effective fire extinguishants. Unfortunately, such compounds hydrolyze readily and are, therefore, toxic. On the other hand, bromine substitution on alkyl or fluoroalkyl groups contained in silicon and siloxane compounds, is likely to provide effective extinguishment without the problem of hydrolysis. Moreover, most siloxanes have low toxicities. No work in this area has been performed, and synthetic work is needed. Note that the chemistry of silicon is well understood and a large number of related silicon compounds are made commercially. It is likely that silicon-containing fire extinguishants would be manufacturable at a reasonable cost.

T Metal Complexes

Transition metal complexes could provide highly effective fire extinguishing agents. For some time, it has been observed that certain metal compounds are very effective in extinguishing flames (Reference 3). For example, iron pentacarbonyl ($\text{Fe}(\text{CO})_5$) may very well be one of the most effective extinguishing agents ever found (Reference 4). Moreover, chromyl chloride (CrO_2Cl_2) appears to be as much as two orders of magnitude more effective than the halons in inhibiting hydrocarbon flames (Reference 5).

Transition metals, are elements that contain incomplete d-block electronic shells in one or more of their compounds and include such elements as iron, chromium, manganese, etc. It may be that these incomplete shells aid in extinguishment by providing new catalytic pathways for oxidation/reduction that eliminate precursors for normal combustion pathways. On the other hand, it may be that particulates are generated within a fire providing heterogeneous pathways for free-radical recombination. Whatever the mechanism is, transition metal compounds appear to be highly effective.

Unfortunately, most transition metal compounds are either highly toxic (such as iron pentacarbonyl and chromyl chloride) or are solids, with no effective method for delivery and three-dimensional dispersion without major hardware changes. However, one large group of transition metal compounds may have the properties needed for effective use as fire extinguishants

and, at the same time, appear to have low toxicities. By using organic ligands containing negative charges whose sum is equal to the positive charge on the central metal ion, neutral transition metal compounds can be prepared. Because the overall complexes are neutral, the compounds are nonionic, a property that gives two important characteristics. (1) In some cases, these are **known** to have a relatively high volatility to aid in providing three-dimensional fire and explosion suppression. (2) All or nearly all of these compounds should be soluble in organic liquids such as hydrofluorocarbons, providing a means for dispersion.

FUTUREWORK

The work on this contract is approximately one-half finished. The establishment of the information storage system and the search for references has been completed, although new references will be added to the database as they become available. The on-going effort to identify additional chemical families, above those already reported, will be continued and new families added to the list of promising chemicals as they are identified. Literature sources will be reviewed to refine the flame and explosion suppression mechanisms already identified. Once the list of promising chemical families has been selected, the preliminary assessment of manufacturability, environmental impact, and toxicity will be made. A final report will then be completed.

REFERENCES

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