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# ADVANCED STREAMING AGENT PROGRAM: CANDIDATE SURVEY

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This report addresses the fire suppression mechanism survey and candidate survey for advanced streaming agents. These surveys led to the identification of chemical families from which an initial list or Broad List of Candidates was developed. The Broad List was comprised of specific chemicals, which were selected by identifying the simplest "parent" molecule within each of the chemical families and making variations of the parent to incorporate desirable features that increase flame suppression capabilities and reduce atmospheric lifetimes. Information on the Broad List was collected focusing on physical/chemical properties, toxicity, manufacturability, environmental issues, and other relevant information. The chemical families identified include brominated alkenes, aromatics, ketones, aldehydes, esters, carboxylic acids, alcohols, ethers, amines, amides, morpholines, and silicon compounds as well as fluoroiodocarbons, metallics, sulfur and sulfur nitrogen compounds, phosphonitriles, epoxides, and nitrosyl compounds. Representative chemicals from each family will be tested for fire suppression capabilities.

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# PREFACE

This report was prepared by the Advanced Protection Technologies (APT) Division, New Mexico Engineering Research Institute (NMERI), The University of New Mexico, Albuquerque, New Mexico 87131-1376 for the Infrastructure Technology Section of Wright Laboratories (WL/FIVCF), Tyndall Air Force Base, Florida 32403-5319, under contract S-5000.7 (NMERI Number 31790) from Applied Research Associates (ARA).

The project Start Date was 27 September 1993, and the End Date is 31 December 1994. The WL/FIVCF Project Officer is Charles J. Kibert; the NMERI Principal Investigator is Stephanie R. Skaggs.





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# EXECUTIVE SUMMARY

## A. OBJECTIVE

This report documents the survey of fire suppression mechanisms and identified candidates for advanced streaming agents.

## B. BACKGROUND

The previous search for "first-generation" halon replacement candidates focused on chemicals that were readily available or would be readily available in the near future and that had a significant amount of toxicological information known. As a result, halocarbon CFC replacements (HCFCs, PFCs, and HFCs) were the major focus as first-generation replacements.

Although the first-generation program was successful in identifying agents, these candidates required approximately 2 to 4 times more agent compared to Halon 1211 and some had toxicological and environmental shortcomings. Consequently, a search for advanced streaming agents became necessary. These advanced agents would be superior in terms of firefighting effectiveness, but would have acceptable environmental effects. The call for highly effective fire extinguishing agents required that the search focus outside the chemical families being investigated as CFC replacements. As a result, under Phase I of the current Advanced Streaming Agent program, a candidate survey was performed, which identified a number of promising chemical families that appear to have desirable firefighting properties.

## C. SCOPE

This report covers Task 2 of Phase I of the Advanced Streaming Agent Program, which addresses the fire suppression mechanism and candidate surveys. Task 2 identifies most of the chemicals that will be investigated throughout the remainder of the effort. The task commenced with a survey of fire suppression mechanisms. Simultaneous to the review of fire suppression mechanisms, a set of selection criteria was established against which all the candidates would be evaluated later in the project. From the fire suppression mechanism survey, an initial list of chemical families was developed. Generally, for each chemical, variations of a parent compound were identified and used to collect information that would be representative of the chemical family. These representative chemicals comprise what is called the Broad List of Candidates.

Information on the Broad List was collected focusing on physical/chemical properties, toxicity , manufacturability, environmental issues, and other relevant information.

## D. METHODOLOGY

Task 2 required a survey of chemical and physical mechanisms of fire extinguishment to determine other fire suppression mechanisms in addition to those used by the current streaming agent. This mechanism survey was performed to identify possible families of chemicals that should be considered in the candidate survey. In addition, a set of selection criteria was established to provide target parameters for candidates. The selection criteria included physical/chemical properties, chemical stability, toxicity, availability/manufacturability and cost, materials compatibility, cleanliness, fire suppression capabilities, and environmental characteristics. These selection criteria and the results of the fire suppression mechanism survey, along with preliminary considerations of identified chemical classes, were used to develop a broad list of prospective candidates for further evaluation as military flightline streaming agents.

## E. APPROACH

Specific candidates were identified based on combining properties that will (or may) enhance flame extinguishment with properties necessary to limit the atmospheric lifetimes, and, thus, limit the global environmental impact of the chemicals.

## F. RESULTS

The survey of fire suppression mechanisms focused on four mechanistic areas: halon-like fire suppression, physical fire suppression, termolecular suppression, and other chemical suppressants. Based on these mechanistic findings, a candidate survey was performed leading to the development of a Broad List of Candidates. The list was derived by combining chemical or structural features that enhance flame suppression with those that diminish atmospheric lifetimes. In many cases, this meant that brominated organic chemicals also had chemical features that lead to a low atmospheric lifetime (i.e., unsaturation or heteroatoms). The chemical families identified include brominated alkenes, aromatics, ketones, aldehydes, esters, carboxylic acids, alcohols, ethers, brominated amines, amides, morpholines, and silicon compounds as well as fluoroiodocarbons, metallics, sulfur and sulfur nitrogen compounds, phosphonitriles, epoxides, and nitrosyl compounds. Specific chemicals were selected within each of these families by identifying the simplest "parent" molecule and making variations of the parent to incorporate desirable features that increase flame suppression capabilities and reduce atmospheric lifetime. This Broad List was intended to be large to allow for later screening of the chemicals on a number

of criteria. For some families (that is, phosphonitriles and sulfur derivatives), non-brominated variations of the parent have not been ruled out until further research indicates that these compounds are not effective fire suppressants.

Readily available information on physical/chemical properties and toxicity pertaining to the chemicals on this Broad List was collected and compiled. Available information was entered into a Microsoft ACCESS® "COMPDS.MDB" database, which is used to store information on advanced agent candidates. All the information in the database is linked to the citation of the source from which the data were derived. Sources for the information include the open literature, other databases, and industry contacts.

Based on availability or ease of synthesis, a representative candidate or two was or will be selected from each chemical family. Representative candidates will be added as research continues or as compounds from the candidate families become available. The candidates will be tested in the laboratory cup burner to determine the extinguishing efficiency representative of the chemical family. The list of representative candidates will be subject to revision as (1) test data are obtained, (2) regulatory, safety, and environmental issues become better defined, (3) assessments of compounds and chemical families are made, and (4) other candidate compounds or families are identified.

## G. CONCLUSIONS

A fire suppression mechanism survey has been completed. The survey reveals several classes of chemicals that hold promise as fire extinguishing agents. Several of these classes of chemicals extinguish flames by mechanisms other than hydrogen radical scavenging, which is the predominant mechanism in halon fire extinguishment.

An important step in selecting advanced streaming agent candidates is the establishment of selection criteria against which compounds will be compared to determine their appropriateness as streaming agents. In this effort, a list of selection criteria was established and targets were set for each of the parameters. Although these criteria are not stringent determiners of which candidates will be selected, they provide guidelines when selecting chemicals.

The chemical families which have been identified during the candidate survey include brominated alkenes, aromatics, ketones, aldehydes, esters, carboxylic acids, alcohols, ethers, amines, amides, morpholines, and silicon compounds as well as fluoroiodocarbons, metal compounds, sulfur and sulfur nitrogen compounds, phosphonitriles, epoxides, and nitrosyl compounds. A representative compound from each chemical class has been or will be selected

based on availability or ability to synthesize and tested in the laboratory cup burner to determine the flame extinguishment efficiency of the chemical class.

## H. RECOMMENDATIONS

It is recommended that testing of the representative candidates from each chemical family commence or continue. This testing is both for determining fire suppression capabilities and for assessing toxicological, chemical, and stability properties. This testing has been outlined in the four-year workplan in Phases I and II.

In addition, it is recommended that the issues relating to cleanliness of candidates agents be clarified, since some of the chemical classes (e.g., metals and silicon compounds) identified may leave minimal or significant residue upon discharge from an extinguisher or during interaction with a fire. Depending on the chemical nature of the residue, cleanliness may not cause a problem under typical use, but further work is needed to resolve this question. Finally, issues relating to toxicity of agents should be defined. Definitive studies specifying toxicity criteria should be performed to determine the level of toxicity that is acceptable in typical use scenarios.

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## ACRONYMS AND ABBREVIATIONS

| | |
|---|---|
| ARA | -- Applied Reseaarch Associates |
| APT | -- Advanced Protection Technologies |
| CAA | -- Chemical Action Agent |
| CAS | -- Chemical Abstract Services |
| CFC | -- Chlorofluorocarbon |
| CCRIS | -- Chemical Carcinogenesis Research Information System |
| DC | -- Direct Current |
| EPA | -- Environmental Protection Agency |
| FC | -- Fluorocarbon (perfluorocarbon) |
| GWP | -- Global-Warming Potential |
| HCFC | -- Hydrochlorofluorocarbon |
| HFC | -- Hydrofluorocarbon |
| HFE | -- Hydrofluoroether |
| HSDB | -- Hazardous Substance Data Bank |
| NIST | -- National Institute of Standards and Technology |
| NMERI | -- New Mexico Engineering Research Institute |
| NRL | -- Naval Research Laboratory |
| NOAA | -- National Oceanic and Atmospheric Administration |
| NTIS | -- National Technical Information Service |
| ODP | -- Ozone-Depletion Potential |
| PA | -- Public Affairs |
| PAA | -- Physical Action Agent |
| PFC | -- Perfluorocarbon |
| RTECS | -- Registry of Toxic Effects of Chemical Substances |
| TCRI | -- Toxic Chemical Release Inventory |
| US | -- United States |
| USSR | -- Union of Soviet Socialist Republics |
| VMS | -- Volatile Methyl Siloxanes |
| WACAM | -- Weighted Attributes Candidates Assessment Matrix |

# SECTION I

# INTRODUCTION

The previous search for "first-generation" halon replacement candidates focused on chemicals that were readily available or would be readily available in the near future and for which a significant amount of toxicological information was known. This strategy was adopted for two reasons: (1) readily available chemicals could be tested, at a reasonable cost and a large-scale, to verify their effectiveness in firefighting scenarios, and (2) toxicological testing of candidates is extremely expensive and time consuming. As a result, CFC replacements were the major focus as first-generation replacements because relatively large quantities of agent were available, often gratis from the producers, and because the manufacturers were supporting the toxicological testing, which was required for CFC replacements. This strategy proved successful and identified a number of candidates readily available for testing and on which a significant amount of toxicity testing had already been performed. Several of the chemicals identified have since been commercialized. Consequently, the Air Force "first-generation" streaming agent program did not require large capital expenditures for agent purchase or toxicity testing.

Although the first-generation program was successful in identifying candidates that were available and did not require toxicological testing, these candidates required approximately 2 to 4 times more agent compared to Halon 1211. Additionally, some had toxicological and environmental shortcomings. Consequently, a search for advanced streaming agents became necessary. These advanced agents should be superior in terms of firefighting effectiveness, but should have acceptable environmental effects. The requirement for highly effective fire-extinguishing agents required that the candidate search focus outside the chemical families being investigated as CFC replacements. The properties needed for effective firefighting were distinct from those required for effective refrigerants, solvents, and foam-blowing agents. As a result, under Phase I of the current Advanced Streaming Agent Testing Program, a candidate survey was performed, which identified a number of promising chemical families that appear to have desirable firefighting properties (Reference 1). In some cases, the literature indicates that some of the chemicals identified require a concentration of less than 1 percent by volume in air to extinguish flames compared to a concentration of approximately 3 percent required by Halon 1211.

This report covers Task 2 of Phase I of the Advanced Streaming Agent Testing Program, which addresses the fire suppression mechanism and candidate surveys. Task 2 was designed to identify the chemicals that should be investigated throughout the remainder of the effort. The task commenced with a survey of fire-suppression mechanisms. Simultaneous to the review of fire-

task commenced with a survey of fire-suppression mechanisms. Simultaneous to the review of fire-suppression mechanisms, a set of selection criteria was established against which all the candidates would be evaluated later in the project. From the fire-suppression mechanism survey, an initial list of chemical families was developed. Generally, for each chemical, variations of a parent compound were identified and used to collect information representative of the chemical family. These representative chemicals comprise the Broad List of Candidates. Information on the Broad List was collected, focusing on items pertaining to physical/chemical properties, toxicity, manufacturability, environmental issues, and other relevant information. Originally, the workplan dictated that these data would be compared to the selection criteria in a Weighted Attributes Candidate Assessment Matrix (WACAM). Through the WACAM process, chemicals were to be selected for further evaluation and testing; however, for many of the chemicals, specific information needed to make the comparison was missing. Therefore, a WACAM was not performed for this report. Instead, a representative candidate from each chemical family was chosen, based on availability, to test flame extinguishment effectiveness.

## SECTION II

## SURVEY FIRE SUPPRESSION MECHANISMS

Task 2 required a survey of chemical and physical mechanisms of fire extinguishment to determine other fire suppression mechanisms besides those used by the current streaming agent. This survey was performed to identify possible families of chemicals that should be considered in the candidate survey. The results of this survey, along with preliminary considerations of identified chemical classes, were used to develop a broad list of prospective candidates for further evaluation as military flightline streaming agents.

Papers and articles dating from 1986 to 1993 were searched using the Chemical Abstract Service (CAS) on-line database. Key words relating to combustion, fire, flame, and radical were used in the search strategy. Literature titles found under the headings that pertained to mechanism or suppression were noted and the abstracts evaluated for applicability. The articles were then collected and synopsized below.

Additional searches were performed on the following authors, who were known to have done work relating to fire suppression.

- Boirdi, Joan C.
- Fristrom, R. M.
- Lazzara, Charles P.
- Papp, John F.
- Safieh, H. Y.
- Vandooren, J.
- Van Tiggelen, P. J.
- Westbrook, Charles K.

In addition, all the articles in the journals *Combustion and Flame* and the *International Symposium on Combustion* from 1984 to the present were searched using the same search strategy as described above. Appropriate articles were collected.

Pertinent information derived from the fire-suppression mechanism survey is summarized below. Since understanding the process of combustion helps in understanding how to disrupt this process, a review of the important features of combustion is presented first.

## A. COMBUSTION MECHANISMS

### 1. Kinetic Reaction Rate Studies

#### a. Hydrogen Radicals

The generation, branching, propagation, and termination of hydrogen radicals are the most important steps in the combustion process. The role of hydrogen radicals in combustion has been extensively researched. Basevich (Reference 2) gives an excellent summarization of the mechanisms in which hydrogen radicals have an active role. This review paper covers the oxidation of hydrogen, methane, methyl alcohol, acetylene, ethylene, ethane, and methyl amine. The paper examines the different elementary reactions and the kinetics of these reactions for the above systems; it contains 264 references, though most of these are of USSR origins.

Using a set of experimental mole fractions from the "burnt gas" region, Goodings and Hayhurst (Reference 3) examined the effect of termolecular reactions on recombination of hydrogen and hydroxyl radicals in fuel-lean reactions.* Reaction [1]

$$H + OH + M \rightarrow H_2O + M^* \qquad [1]$$

predominates in and close to the reaction zone; however, at distances farther from the flame, Reactions [2] and [3] work catalytically to achieve the same results.

$$H + O_2 + M \rightarrow HO_2 + M^* \qquad [2]$$

$$OH + HO_2 \rightarrow H_2O + O_2 \qquad [3]$$

Reactions such as [1] and [2] could be relevant in identifying materials for fire suppression. The importance of termolecular recombination in reducing free radicals has superficially been studied, but no firm conclusions have been reached on the overall impact that these types of reactions have on fire suppression (see also related References 4, 5, 6, and 7).

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* Here and throughout this report, M represents a neutral (third-body) species and M* represents M when kinetically or vibrationally activated.

b. Hydroxyl Radicals

References 2 and 3 both consider the importance of radical reactions of hydroxyl free radicals in combustion. In simple hydrogen-oxygen combustion system radicals, hydroxyls are the products in two important chain branching reactions ([4] and [5]):

$$H + O_2 \rightarrow OH + O \qquad [4]$$

$$H_2 + O \rightarrow OH + H \qquad [5]$$

In Reaction [4], note particularly that the two products are important to the initiation of oxidation of hydrocarbons. Interruption of this process is a key to effective fire suppression. Bott and Cohen (Reference 8) have measured and deduced some of the recombination pathways for hydroxyl radicals with methyl radicals in shock tube experiments. They do not draw many conclusions from the data except that direct recombination to form methyl alcohol predominates in the temperature range from 298-1200 K. The free radical recombination observed is significant because it acts as a termination step in the chain reaction. Dunlop and Tully (Reference 9) and Oldenborg et al. (Reference 10) have extended and refined the work of several authors including Vaghjiani (Reference 11) and Sworski (Reference 12) in kinetic studies of OH radicals with hydrogen and methane. Neither Reference 8 nor 9 is a significant work in hydroxyl reaction kinetics, but each demonstrates the most recent studies being performed in the field.

One of the more important reactions of hydroxyl radicals is the contribution they make in reducing ozone-depleting materials. In a short note, Cooper (Reference 13) estimates—by using semi-empirical and *ab initio* calculations—the lifetimes of hydrofluorocarbons versus hydrofluoroethers in the atmosphere. This methodology holds some promise in predicting new fire suppressant materials, by allowing quick screening of molecules. In this study, hydrofluoroethers (HFE) exhibit shorter lifetimes in the atmosphere than hydrofluorocarbons in general. Therefore, HFEs have less potential for depleting the ozone. Also apparent in this modeling study is the ability to view the importance of the placement of certain chemical structures in a molecule, which affects the combustion suppression effectiveness and the atmospheric lifetimes.

Another *ab initio* study by McKee (Reference 14) purports that hydroxyl radicals form a complex with dimethyl sulfide ($CH_3SCH_3$). The complexation of radicals will slow the overall oxidation reaction and allow radical suppression mechanisms to dominate the process (see also related References 15, 16, and 17).

c. Hydrocarbon Fuels

Basevich (Reference 2) and Walker (Reference 18) offer two thorough recent reviews of hydrocarbon fuel combustion. Basevich only details certain systems (methane, acetylene, ethylene, ethane, and methanol), while Walker provides a more general approach in a paper that has 26 references. Chemical kinetic modeling of hydrocarbons containing one to eight carbons have been presented by Westbrook (Reference 19). He relates the importance of the number and placement of the hydrogens of the different isomers of the hydrocarbons, the identification of product distributions for decompositions of fuel and alkyl radicals, and the coupling between large molecule reactions with those of the $H_2$ - $O_2$ - CO reaction, basic to the modeling process. This article presents an overview of the complexity of modeling simple but large hydrocarbon fuels in the combustion process. Mechanisms and kinetics involved in fuel-rich methane flames are reviewed by Burgess and Langley (Reference 20). Two papers report the importance of unsaturation in slowing combustion processes. Walker and Stothard (Reference 21) and Slagle et. al. (Reference 22) both report on the oxidation of unsaturated free radicals with molecular oxygen. The articles contribute to the general kinetic data available on reaction rates for specific elementary reactions present in hydrocarbon combustion. Finally, a measurement of the peroxy-hydroperoxy radical isomerization was undertaken by Hughes et al. (Reference 23) and is important in the critical rate determining step for alkane oxidation (see also related References 17, 24, 25, 26, and 27).

2. Other Rate Parameters

Other factors also contribute to the initiation, propagation, and termination of combustion. Specifically, termination of combustion is affected by heat loss in heating an agent, heat transfer out of the reaction zone, and separation of fuel and flames (Reference 28). Dilution of the fuel or oxidizer also encourages the termination of combustion.

## B. SUPPRESSION MECHANISMS

1. Halons, CFCs, HCFCs, HFCs, and PFCs

Classically, fire suppression requires disrupting one of the three legs of the fire triangle — fuel, heat, and oxygen. Interrupting one of these three legs is the mechanism of all Physically Active Agents (PAA). On the other hand, the primary extinguishment mechanism for Chemically Active Agents (CAA) is chemical or catalytic disruption of the combustion process. Halons and many other bromine- or iodine-containing compounds are considered CAAs. Chlorofluorocarbons (CFC), hydrochlorofluorocarbons (HCFC), hydrofluorocarbons (HFC), and

perfluorocarbons (FC) are considered PAAs. Note that those designations indicate only the principal mechanism for extinguishment. For example, work at the Naval Research Laboratory (NRL) indicates that Halon 1301 extinguishment of n-heptane is approximately 20 percent physical and 80 percent chemical (Reference 29). The analysis also indicates that about 25 percent of the extinguishment is due to the $CF_3$ group, and about 55 percent is due to the bromine.

a. Chemical Fire Suppression Mechanisms

The accepted mechanism for suppression of fire by halons is catalytic scavenging of hydrogen radicals by a halogen atom or halogen containing molecular fragments. An example of this is the use of $CF_3Br$, Halon 1301, in many fire extinguishment applications. The carbon-bromine bond reacts homolytically to form $CF_3$ radical and hydrogen bromide (Reaction [6]). The hydrogen bromide formed can then react with another hydrogen radical (Reaction [7]). The bromine atoms found in this reaction can then combine to form $Br_2$ (Reaction [8]). $Br_2$ can then react with more hydrogen atoms (Reaction [9]).

$$CF_3Br + H \rightarrow CF_3 + HBr \quad [6]$$

$$H + HBr \rightarrow H_2 + Br \quad [7]$$

$$Br + Br + M \rightarrow Br_2 + M^* \quad [8]$$

$$Br_2 + H \rightarrow HBr + Br \quad [9]$$

Reactions [6] and [7] are sufficiently rapid that they remove hydrogen radicals before they can react as in Reaction [4]. This leaves a much less reactive bromine radical, which will not cause chain branching reactions that promote combustion (Reference 30). Bromine- and iodine-containing compounds (and, to a significantly lesser extent, chlorine-containing compounds) are believed to react by essentially the same mechanism, but detailed kinetic studies for many compounds have not been performed. In a very early report, Creitz (Reference 31) reports on the inhibition of diffusion flames by methyl bromide and trifluoromethyl bromide. His study notes a difference in applying the inhibitor to the fuel and oxygen sides of the reaction. $CH_3Br$ and $CF_3Br$ act as inhibitors when applied to the oxygen side of the reaction, with $CF_3Br$ being significantly better. When applied to the fuel side of the fire, $CF_3Br$ is still a very good suppressant, but $CH_3Br$ can act as a fuel when sufficient oxygen is present. The fact that $CF_3Br$ is a better suppressant than $CH_3Br$ is probably due to the formation of HF, which ties up some of the hydrogen free radicals. Ionization of $CF_3Br$ in hydrocarbon

flames is covered by Morris et al. (Reference 32). They find no evidence that $CF_3Br^+$ is formed or that any ionic process would release bromine atoms. However, work at the University of New Mexico indicates formation of $CF_3Br^+$ (Reference 33). The $CF_3^+$ ion does not react with $H_2$ or $CH_4$, but the ion will react with higher alkanes and alkenes (Reference 34).

b. Physical Fire Suppression Mechanisms

As previously discussed, PAAs disrupt the legs of the classical fire triangle. The primary method of action of these first-generation halon replacements appears to be the absorption of heat into the vibrational modes of the molecule and subsequent disruption of the chemical bonds. The various free radicals produced by the physical destruction of agents such as HCFC-123 or FC-6-1-14 appear to react in a noncatalytic fashion with combustion chain radicals to produce such toxic byproducts as hydrogen fluoride (HF) and carbonyl fluoride ($COF_2$).

Other PAAs such as water mists (remove heat by vaporization) or foams (remove heat and separate oxygen from fuel) interact by a variety of mechanisms. Dry chemical fire-suppression agents may work only by physical mechanisms or may have additional chemical components in their fire-suppression mechanisms. Work under this project will include efforts to distinguish chemical and physical fire-suppression mechanisms and to develop models for predicting the relative importance of these mechanisms in the functional application of new agents.

Karra and Senkan (Reference 35) show that the two most likely initial reactions in the combustion of $CH_3Cl$ are Reactions [10] and [11].

$$CH_3Cl \rightarrow CH_3 + Cl \qquad [10]$$

$$CH_3Cl + Cl \rightarrow CH_2Cl + HCl \qquad [11]$$

The two carbon radicals, $CH_3$ and $CH_2Cl$, are stable both to molecular oxidation and to recombination to form $C_2H_6$, $CH_2ClCH_2Cl$, and $CH_3CH_2Cl$. Also important in radical removal in this system are the Reactions [12] and [13].

$$CH_3Cl + H \rightarrow CH_3 + HCl \qquad [12]$$

$$CH_3Cl + H \rightarrow CH_2Cl + H_2 \qquad [13]$$

Both of these reactions scavenge hydrogen radicals and leave the much less reactive carbon centered radicals. Chlorotrifluoromethane ($CF_3Cl$), inhibits the reaction of $H_2$ and $O_2$ below 1500 K through a mechanism similar to Reaction [12] (Reference 36). The $CF_3$ radical undergoes further reaction with $H_2$ to regenerate hydrogen radicals, but this process is very slow compared to the initial hydrogen scavenging reaction. Hidaka and Suga (Reference 37) have found that $CF_3Cl$, at higher temperatures, acts as a promoter for methane and through a different mechanism acts as an inhibitor in ethylene combustion.

Fletcher (Reference 38) has studied the combustion of fluorocarbons under several conditions. Only under stringent conditions of addition of fluorine and/or chlorine trifluoride has combustion occurred. Since these experiments used fluorine as an oxidizer, direct correlation to an oxygen system is sketchy. Higher chain fluorocarbons cleave at lower temperatures than the shorter chains. Carbon-carbon bond cleavage dominates these reactions until only inert $C_2F_6$ molecules are left or the reaction molecules pass through the reaction zone. This mechanism of decomposition can be exploited to deliver inert materials that can effectively suppress combustion by heat dissipation.

Rate constants for reactions of two HCFCs ($CH_3CFCl_2$ and $CH_3CF_2Cl$) and one HFC ($CH_2FCF_3$) with hydroxyl free radicals have been analyzed (Reference 39). Rate constants for single reaction steps can give an estimate of the overall reaction rate. A decrease in the reaction rate for a step in the combustion process can slow or terminate the chain reaction. The reaction of $CH_3CFCl_2$ with hydroxyl does display an anomaly from the other reactions. At lower temperatures, Reaction [15], which involves a product of Reaction [14], competes effectively for OH. In the case of the other two compounds, no such competing reaction is apparent, and only Reactions [16] and [17] are observed (see also related References 40, 41, and 42).

$$OH + CH_3CFCl_2 \rightarrow H_2O + CH_2CFCl_2 \qquad [14]$$

$$OH + CH_2CFCl_2 \rightarrow \text{ products} \qquad [15]$$

$$OH + CH_3CF_2Cl \rightarrow H_2O + CH_2CF_2Cl \qquad [16]$$

$$OH + CH_2FCF_3 \rightarrow H_2O + CHFCF_3 \qquad [17]$$

c. Suppression Effectiveness

Judging the ability of a material to suppress combustion is a very difficult task because of the lack of good models and reproducible data from combustion tests for all the materials of interest. Although empirical methodology is the only accurate means to test suppression, attempts to model fire suppression effectiveness have been made (Reference 43, pgs. 28 and 36). Modeling by Borisov (Reference 44) on the effect of *promoting* agents on ignition could be used to evaluate materials by looking for impotent promoters. The technique predicts efficiency using kinetic parameters in both analytical and numerical solutions.

The effectiveness of halons has usually been explained in terms of the effectiveness of a halogen group to remove hydrogen from the combustion process catalytically. Two papers also seem to indicate that other factors could be important in the extinguishing process. Morris (Reference 32) indicates that $CF_3$ radical reacts with the fuel. This reaction would likely reduce the flammability of the fuel. Huie, Kurylo, and Zhang (Reference 39) note that $CH_3CFCl_2$ is a very effective OH scavenger, even at lower temperatures.

d. Unexplained Suppression Forces

When modeling of halons, CFCs, HCFCs, HFCs, and PFCs is performed and compared to empirical data, the empirical data tend to outperform the predicted values for suppression (Reference 43). The correlation for this has not yet been fully explored, but at least two possibilities might explain the added effectiveness of these materials.

An important set of reactions in combustion chemistry is the effect of termolecular recombination on inhibition. This mode depletes the active H, O, and OH radicals and stops the chain branching and propagation steps. Vinckier and Christiaens (Reference 45) report that the rate constants for Reaction [18], increase with temperature. Similar effects (i.e., Reactions [19] and [20]) from neutral molecules and fragments present from halon decomposition suppress branching and propagation steps. Trifluoromethane ($CF_3H$) forms from the reaction of the trifluoromethyl radical and hydrogen radicals. Once formed, it is an unreactive species and acts as a termolecular agent.

$$Mg + O_2 + M \rightarrow MgO_2 + M^* \qquad [18]$$

$$H + CF_3 + M^* \rightarrow CF_3H + M^* \qquad [19]$$

$$H + H + CF_3H \rightarrow H_2 + CF_3H \qquad [20]$$

Pimblott (Reference 46) observes that in aqueous systems, electron scavengers are cooperatively aided by chemicals that expressly remove excess OH. In a flame, similar reactive agents are present in the form of hydrogen, oxygen, and hydroxyl radicals. Agents that effectively and catalytically remove both hydrogen and either oxygen or hydroxyl radicals from flames can be expected to show synergistic effects on suppression (see also related Reference 47).

2. Other Chemical Suppressants

a. Dry Powder

Dry powder extinguishers are some of the most effective fire suppressants (Reference 48). Sodium bicarbonate, $NaHCO_3$, has been shown to be 20 times more effective than $CF_3Br$ on a weight percent basis (Reference 43, pg. 70). Recombination reactions at the surface of the particles and in the gas phase (from the vaporized metal atoms) have been suggested as mechanisms to explain the effectiveness of these agents. Most researchers agree that the $\mathcal{M}OH$ intermediate, where $\mathcal{M}$ is a metal atom, is critical in the removal of hydrogen radicals through Reaction [21].

$$\mathcal{M}OH + H \rightarrow H_2O + \mathcal{M} \qquad [21]$$

The order of effectiveness for alkali metal dry powders is oxalate > cyanate > carbonate > iodide > bromide > chloride > sulfate > phosphate with the metal being ranked rubidium > potassium > sodium > lithium (Reference 43, pg. 71).

Amrogowicz and Kordylewski (Reference 49) report on the relative effectiveness of sodium bicarbonate ($NaHCO_3$), ammonium dihydrogen phosphate ($NH_4H_2PO_4$), and calcium carbonate ($CaCO_3$) for suppression of dust explosions. Two of the agents ($NaHCO_3$ and $NH_4H_2PO_4$), proved more effective than the $CaCO_3$, which is often used as a suppressant. Chemical action by the two agents was cited for the improvement in explosion suppression. Unfortunately, no further elaboration as to the exact nature of the chemical action was made.

b. Water Additives

Use of alkali metal inhibitors in a water spray may adequately combine the ease of aerosol technology with the enhanced suppression effectiveness of the dry powder compounds. Many of the compounds referred to above are soluble in water, and they can be nebulized into an aerosol spray of known inhibitor concentration containing particles of certain

size. This ability to deliver a mix of molecularly dispersed inhibitor and particle size inhibitor could be advantageous due to the conflicting information concerning inhibition mechanism (Reference 43, pg. 71-73). Augmenting these properties is the fact that mixtures of materials that scavenge both H and OH radicals could be easily delivered.

c. Miscellaneous Materials

Transition metal, silicon, germanium, phosphorus, and sulfur compounds have all been studied to some degree to explore suppression effectiveness. A thorough review of this testing is covered in the *NIST Technical Note 1279* (Reference 43, pg. 61-74). In an article by Zachariah (Reference 50), the introduction of sulfur compounds into $H_2/O_2$ flames lowers the propagation velocity, suggesting decreases in radicals; this lowering is attributed to the catalytic effect of sulfur dioxide on the radical chain carriers. Finally, exfoliated vermiculite has been tested for extinguishing liquid hydrocarbon fires (Reference 51). Vermiculite is a particulate mineral that is non-combustible, nonabrasive, non-irritant, moldable, and chemically inert. The tests successfully extinguished fires up to 4500 $cm^2$ in area (see also related References 52, 53, and 54).

3. Physical Suppressants

a. Magnetics

A few short papers on the subject of use of magnetic fields have recently been published. Ueno (Reference 55) has used a magnetic field of 0.5 -2.2 Tesla to contain and smother a small flame.

A "magnetic curtain" blocks the flow of air in and out of the contained space. Wakayama (Reference 56) has been able to control combustion in diffusion flames by using magnetic fields to regulate the flow of air. No other information as to how effective this technique is with turbulent flames has been published.

b. Electricity

Strong evidence has been presented on fire suppression by a DC electric field (Reference 57). Corona discharge generated by the DC field has been used to extinguish pool flames of isopropanol. Although the field does generate ions that might be chemically active and ameliorate the radical reactions, the effect seems to be purely aerodynamic. A thin

wire moving parallel to the surface of the pool flame is the most efficient device for flame extinction.

## C. PROPOSED CHEMICAL SUBSTANCES FOR FIRE-SUPPRESSION TESTING

### 1. Halon-Like Chemicals

Many of the materials that are derivatives of halons, CFCs, HCFCs, HFCs, and PFCs have been recommended by NIST in their exploratory list of chemicals for halon substitutes. Even by eliminating CFCs, HCFCs, HFCs, and PFCs from consideration, the NIST report still lists over 40 specific chemicals in several chemical families. The families include halogenated ethers, ketones, anhydrides, esters, unsaturated hydrocarbons, and related thio- and amido- compounds. Interestingly, one compound that also fits this general category of halon-like chemicals, but is not listed by NIST, is hexafluoroepoxypropane. Most epoxy compounds are highly reactive and flammable, but hexafluoroepoxypropane is a non-flammable gas (Reference 58).

### 2. Non-Halocarbon Chemicals

Fire suppression agents that are non-halogenated could solve the problems associated with ozone depletion in the atmosphere. Such agents are referred to here as *advanced agents*. Emulation of the radical scavenging mechanism of halons for combustion suppression is a plausible course of action for new fire extinguishing agents. To achieve this, the material must be able to form radicals easily. Several classes of chemical will be thermally decomposed through the use of a radical mechanism. Some chemical families that might have latent potential are disulfides, azo and azido compounds, and phosphazenes. Some exploratory work using sulfides and sulfur compounds in fire suppression logically allows the extension to disulfides for suppression studies. Azo- and azido- groups are usually thermally unstable and form free radicals upon decomposition. No research into the effectiveness of these materials has been recently published. Phosphazenes, particularly poly(phosphazenes), are temperature resistant materials that are relatively inert. The strong phosphorus-nitrogen bonds present in the compound could be utilized in aiding delivery of the chemical into a large or hot fire before decomposition. Phosphorus and nitrogen compounds are good radical centers and have shown tendencies to be effective extinguishing agents.

### 3. Water Soluble Suppressants

This last section addresses the possibility of using solids or high-boiling liquids that are soluble in water as suppressants. Generally, the idea is to pick chemicals that combine the best suppression effects found in dry powders with the delivery systems offered by using water. The first set of chemicals considered should be dry powder materials that are soluble in water. After that, the possible materials are too extensive to discuss individually, but examples of likely candidates will be described. Sodium metaphosphate, $(NaPO_3)_x$ where x is 2 or more, is a water-soluble chemical used a water softener. The introduction of phosphates into dust explosions drastically reduces the explosion limits through combustion suppression. Sulfur dioxide ($SO_2$) is a fire suppressant (Reference 50), and potassium metabisulfite is a water soluble source of $SO_2$. No information on the effectiveness of these types of material was found in the literature.

## D. SUMMARY

In addressing halon replacements that do not include CFCs, HCFCs, or FCs, consideration has been given to three broad areas of chemicals. The chemicals presented are not meant to represent an exhaustive search and evaluation of specific chemicals, but to give some general suggestion of new materials for suppression testing. Few or no active research programs concerning these chemicals have been published in the recent literature.

The first category is that of halon-like materials (replacement agents). The potential of these materials is in retaining the fire-suppression capabilities inherent in the halocarbons while making them less destructive to the ozone layer. Non-halocarbon chemicals (advanced agents) would eliminate or lessen the hazard to the environment, but issues such as toxicity, materials compatibility, and suppression effectiveness must be considered in their use as replacements to halon. Finally, water soluble or deliverable materials could combine enough of the criteria imposed by fire suppression and environmental concerns to be considered as suitable substitutes for halons.

## SECTION III

## ESTABLISHMENT OF SELECTION CRITERIA

Once the fire suppression mechanism survey identified a number of mechanisms for flame extinction, the next step was to establish the selection criteria to which the candidates would be compared. These criteria or attributes of streaming agent replacements provide target parameters for candidates and include physical/chemical properties, chemical stability, toxicity, availability/manufacturability and cost, materials compatibility, cleanliness, fire suppression capabilities, and environmental characteristics. Several of these selection criteria categories have more than one component. For example, in considering physical properties, some properties relate more to deliverability (boiling point, liquid density, and vapor pressure), while other properties relate to extinguishing ability (vapor heat capacity and heat of vaporization). Therefore, it may be advantageous to consider several physical properties in the WACAM. This is also true for toxicological attributes, where many potential toxic effects (short- and long-term) would need to be considered to assess the health and safety of prospective agents. Likewise, environmental characteristics consider ozone-depletion effects as well as global warming and atmospheric lifetime since these parameters are becoming of increasing importance. The list of selection criteria is presented in Table 1.

TABLE 1. STREAMING AGENT SELECTION CRITERIA.

| Category | Specific Criterion | Target |
|---|---|---|
| Physical properties | Boiling point | > -10 °C |
| | Melting point | < -60 °C |
| | Vapor pressure | Sufficient for evaporation (≅1 kPa) @ 0 °C |
| Chemical stability | Thermal decomposition | < 1% decomposition per year @ 125 °C |
| Toxicity | Acute | Most sensitive toxic endpoint threshold > extinguishing concentration |
| | Chronic | Non-carcinogenic |
| Manufacturability | Availability | Known synthetic routes |
| | Cost | < $50/lb |
| Cleanliness | Corrositivity | Non-corrosive @ 125 °C |
| | Electrical conductivity | Agent and decomposition products not electrically conductive |
| Extinguishing effectiveness | Cup-burner concentration | ≤ Halon 1211 (≅ 3 % vol) |
| Environmental characteristics | Atmospheric lifetime | < 1 year |
| | Ozone-depletion potential | < 0.001 |

# SECTION IV

# SURVEY OF CANDIDATES

After the fire-suppression mechanism survey was performed and the streaming agent selection criteria were established, a candidate survey was carried out that identified a number of chemicals for further evaluation. The candidate survey commenced with the development of a Broad List of chemicals, based on the fire suppression mechanism review and an initial assessment of the chemical classes identified from this review. Information on the candidates was collected by performing on-line CAS searches. This information was compiled in a Microsoft ACCESS® database. Many of the chemicals had large gaps in the data necessary to perform the WACAM process; therefore, a representative candidate was selected from each chemical family based on availability. These representative chemicals are recommended for testing to determine whether the family has fire-suppression properties.

## A. RATIONALE FOR CHEMICAL FAMILIES

The approach taken to identify specific candidates was based on combining properties that will (or may) enhance flame extinguishment with those properties necessary to limit the atmospheric lifetime, and, thus, limit the global environmental impact of the chemicals. Chemical features that are known to or may enhance flame extinguishment include:

- Bromine
- Iodine
- Metals
- *Sulfur**
- *Phosphorus*
- *Epoxides* (/ O \)
- *Nitrosyls* (NO)

Bromine and iodine are known to provide effective fire extinguishment (Reference 59). Transition metals, in particular iron compounds, are also know to be effective flame extinguishants. Of these three, iodine and metals will almost certainly lead to low atmospheric lifetimes. Thus, for only bromine-containing compounds will additional groups that lower the atmospheric lifetimes need to be considered (i.e., tropodegradable substituents). Phosphorus-containing materials are used as flame retardants in fabrics and may provide flame extinguishing

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* Italics indicate features suspected of having the designated influence.

ability, in some cases. Nitrosyl, epoxides, and sulfur compounds potentially produce free radicals that presumably could disrupt combustion chain reactions.

Tropodegradable substituents may act in one (or more) of five ways to reduce the atmospheric lifetimes of molecules: (1) reaction with hydroxyl free radicals (OH), (2) photodecomposition, (3) rainout, (4) thermal decomposition, or (5) hydrolysis due to atmospheric mosture. Chemical features that are known to or may reduce atmospheric lifetimes through these mechanisms include:

Reaction with Hydroxyl Free Radicals (Unsaturated Compounds)

- Unsaturated double bonds (C=C)
- Aromatics

Rainout (Polar Compounds)

- Carbonyl groups (–C(O)–)
- Hydroxyl groups (OH)
- *Ether linkages** *(–O–)*
- *Amines, amides, and morpholines*

Photodecomposition

- Iodine

Thermal Decomposition and/or Hydrolysis

- *Epoxides* (/ O \)
- Metals
- Phosphorus
- Sulfur
- Silicon
- Nitrosyls

1. Bromine Compounds

Because bromine itself does not impart a low atmospheric lifetime, brominated compounds must contain other functional groups that yield short lifetimes. Bromine attached directly to silicon, phosphorus, and sulfur will likely result in highly toxic chemicals. Fluorobromoalkyl groups such as $-CF_2Br$ may avoid toxicity problems. Other fluorobromoalkyl

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* Italics indicate features suspected of having the designated influence.

groups may also be considered. Attaching brominated components to tropodegradable substituents should lead to global environmental acceptability.

a. Compounds with Unsaturated Double Bonds (Alkenes)

Alkenes have very short atmospheric lifetimes, but tend to be toxic. Toxicity is reduced if the halogen atoms are kept away from the double bonds. Carcinogenicity and mutagenicity are of concern when the halogens are in the $\alpha$ and $\beta$ positions.

b. Aromatics

Like the alkenes, the aromatics contain unsaturated bonds and are expected to react with hydroxyl free radicals in the atmosphere. They are, however, less reactive and, because of this lower reactivity, may have unacceptable atmospheric lifetimes. Derivatives of perfluorobenzene such as pentafluorobromobenzene or pentafluoro(difluorobromomethyl)—benzene would be considered.

c. Compounds with Carbonyl Groups (Ketones, Aldehydes, Esters, Carboxylic Acids)

The presence of a carbonyl group (–C(O)–) greatly increases the potential for rainout and slightly increases the potential for photolysis. Carboxylic acids tend to be corrosive and, possibly, have high toxicities. For this reason, carboxylic acids are not given a high priority for investigation.

Bromine atoms are best kept away from the carbonyl group, for $\alpha$ and (probably) $\beta$ carbonyl compounds tend to be lachymators and have a high toxicity. For this reason compounds that have the halogen in the $\gamma$ position, such as $HC(O)CH_2CH_2CF_2Br$ and $HC(O)OCH_2CF_2Br$, should be considered. Note, that a relatively high proportion of hydrogen atoms on the molecules can lead to flammability.

d. Compounds with Hydroxyl Groups (Alcohols)

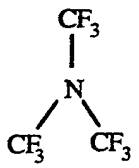
Like the carbonyl group, the presence of an OH substituent will enhance rainout. These compounds will have a low atmospheric lifetime. Again, bromine (and probably fluorine) atoms should be kept away from the hydroxy group to decrease the toxicity. Possible compounds include $HOCH_2CF_2Br$.

e. Ethers

Of all the polar compounds, ethers are likely to be the least toxic. Unfortunately, ethers are also the least polar, resulting in longer atmospheric lifetimes. Work at the US Environmental Protection Agency (EPA) Air and Energy Engineering Research Laboratory (Research Triangle Park, NC) indicates an unacceptably long atmospheric lifetime for many polyfluorinated ethers. Possible compounds would be of the form $F_3C$-O-R where R = $CF_2Br$ or $CF_2CF_2Br$. Alternatively, brominated groups could be on either side of the ether linkage, i.e., $CF_2Br$-O-$CF_2Br$.

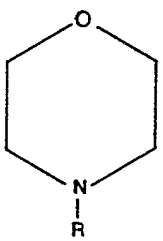
f. Amines, Amides, and Morpholines

Most amines and amides are pyramidal with a lone pair of electrons, making them polar and subject to rainout from the atmosphere. Examples are ammonia ($NH_3$) and trimethylamine ($N(CH_3)_3$), the molecules of which are shaped like pyramids. Surprisingly, however, tris(trifluoromethyl)amine is trigonal planar:




The lone pair of electrons on tris(trifluoromethyl)amine has become sterically inactive. This feature, which may result from electron withdrawl by the highly electronegative fluorine atoms and which appears to be present for all highly fluorinated alkyl substituents, gives the molecule both good and bad properties. First, the chemical is low in toxicity, but it is also less polar than most amines, decreasing its ability to rainout. Brominated derivatives of tris(trifluoromethyl)amine where one or more of the trifluoromethyl groups is replaced with -$CF_2Br$ would be considered.

A related series of compounds is the perfluoromorpholines, which are fluorinated N-alkylmorpholines where morpholine is tetrahydro-p-isoxazine:

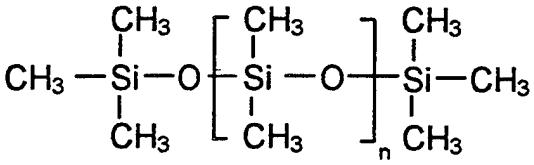


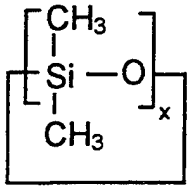
These materials have low toxicities and are non-flammable. To date, however, indications are that these compounds will receive the same regulatory treatment as perfluorocarbons since there are indications that the atmospheric lifetimes are long. 3M Company now markets three perfluoromorpholines — PF-5052 (perfluoro-N-methylmorpholine), PF-5062 (perfluoro-N-ethylmorpholine), and PF-5072 (perfluoro-N-isopropylmorpholine) — as part of their "Fluorinert Liquids" line of products. The commercialized materials have relatively high boiling points, ranging from 50 to 95°C. Bromine-substituted compounds could provide excellent fire extinguishants.

g. Silicon Compounds

The silicon-halogen bond generally confers a high toxicity to molecules due to the capability for hydrolysis (to give hydrogen halides). Thus, only compounds where silicon is attached to atoms other than halogen (e.g., oxygen, carbon, hydrogen, and nitrogen) will be considered. Note, however, that Si-H bonds often lead to spontaneously flammable compounds. The presence of silicon will decrease the atmospheric lifetime compared to carbon compounds, because silicon bonds tend to be weak (increasing the probability of thermal degradation) and because of mechanistic pathways based on valence shell expansion. Silicon-containing compounds will lead to the combustion byproduct silicon dioxide ($SiO_2$), and, therefore, silicon compounds may not be clean.

One family of silicon compounds that will be considered are the partially brominated alkylsilanes, which includes such chemicals as $R_3Si\text{-}CF_2Br$. The akyl groups, R, may be perfluorinated. Another family are partially brominated siloxanes, which contain the Si-O-Si group. One example of the parent, nonbrominated derivatives are the polydimethyl-siloxanes, which contain the group $[\text{-}Si(CH_3)_2\text{–}O\text{–}]$. These materials have very low toxicity and are liquids at room temperature. However, they tend to be oils with relatively low vapor pressures and could leave residue after discharge. Volatile methyl siloxanes, however, have higher vapor pressures than most other siloxanes. Cyclic and linear volatile methyl siloxanes (VMS) are either linear or cyclic and have the general structures shown below, where "n" or "x" is an integer giving the number of repeating units.





Of particular importance is that the atmospheric lifetimes are between 10 and 30 days (Reference 60), and they have a zero ODP. The compounds are marketed (as cleaning materials) by Dow Corning Corporation. Properties of these materials are shown in Table 2. One or more of the methyl groups could be replaced by $-CF_2Br$ groups. The atmospheric lifetimes would be low.

TABLE 2. VOLATILE METHYL SILOXANES MARKETED BY DOW CORNING CORPORATION.

| | OS-10 | OS-20 | OS-30 | OS-70 | OS-80 | OS-90 |
|---|---|---|---|---|---|---|
| Compound | Hexa-methyl-disiloxane | Octamethyl-trisiloxane | Decamethyl-tetrasiloxane | Octamethyl-cyclotetra-siloxane | Octamethyl-cyclotetra-siloxane; decamethyl-cyclopenta-siloxane | Decamethyl-cyclopenta-siloxane; dodecamethyl-cyclohexa-siloxane |
| Flash Point, closed cup, °C (°F) | -1 (30) | 34 (94) | 57 (135) | 55 (131) | 52 (125) | 74 (165) |
| Boiling point, °C (°F) | 100 (212) | 149 (300) | 192 (378) | 172 (342) | 177 (351) | 217 (423) |
| Evaporation rate (n-Butyl Acetate = 1.0) | 3 | 1 | 0.1 | 0.2[a] | 0.18 | 0.04 |
| Viscosity at 25 °C (77 °F), cSt | 0.65 | 1.0 | 1.5 | 2.5 | 2.5 | 5.0 |
| Specific gravity at 25 °C (77 °F) | 0.761 | 0.82 | 0.85 | 0.95 | 0.95 | 0.96 |
| Surface tension at 25 °C (77 °F), dynes/cm | 15.9 | 16[a] | 18 | 17.8 | 19.0 | 21 |
| Freezing point, °C (°F) | -68 (-90) | -82 (-115)[a] | -76 (-105) | 17 (62) | 15 (59) | -44 (-47) |
| Heat of vaporization at 65 °C (150 °F), cal/g[a] | 46 | 44 | 36 | 40 | 38 | 25 |

[a]Estimated.

2. Iodine Compounds

Iodine, as with bromine, is known to disrupt the combustion chain reactions, which leads to its superior flame extinguishment properties. In addition, iodine compounds are photolytically active, which leads to short atmospheric lifetimes.

A recent paper from NOAA (National Oceanic and Atmospheric Administration) states that

> ...the extremely short lifetime of $CF_3I$ greatly limits its transport to the stratosphere when released at the surface, especially at midlatitudes, and the total anthropogenic surface release of $CF_3I$ is likely to be far less than that of natural iodocarbons such as $CH_3I$ on a global basis. It is highly probable that the steady-state ozone depletion potential (ODP) of $CF_3I$ for surface releases is less than 0.0008 and more likely below 0.0001. Measured infrared absorption data are also combined with the lifetime to show that the 20-year global warming potential (GWP) of this gas is likely to be very small, less than 5. Therefore this study suggests that neither the ODP nor the GWP of this gas represents significant obstacles to its use as a replacement for halons (Reference 61).

It should be noted that the likely ODP is actually less than that determined for some of the hydrofluorocarbons (HFC), which are usually given a nominal ODP of zero (Reference 62).

The most promising agents are the simple fluoroalkyl iodides, e.g., $CF_3I$, $CF_3CF_2I$, etc. Cyclic compounds such as perfluorocyclobutyl iodide could also be included. Complicated iodine-containing molecules may hold an advantage in decreasing the toxicity. Radiological opaquing agents are often iodinated and non-toxic. However, allergic sensitization to these types of compounds may be a complication to using these materials in radiology. Iodine-containing biomolecules may provide insight into other low toxicity chemicals. Significant work on iodine compounds has already been performed under this program (Reference 63).

3. Metal Compounds

Iron pentacarbonyl and other iron compounds are known to be good flame extinguishants (Reference 64). This is likely due to the partially filled d subshells, which enables catalytic activity in oxidation-reduction reactions. Manganese and cobalt, which are chemically

similar to iron, may also provide effective extinguishing ability; however, such materials are often expensive. The toxicity of metal compounds is often imparted by the attached groups rather than by the metal atom. Metal carbonyls are toxic; however, the toxicity of metal nitrosyls may be more acceptable and could have an added extinguishing ability from the nitrosyl group. Bis(cyclopentadienyl) iron (II), also known as ferrocene, has a very low toxicity, but flammability may be a concern. Although it is a solid, it has a relatively high vapor pressure (for a solid). The perfluorinated derivative may have an even higher vapor pressure and may not be flammable. Since cyclopentadienyl derivatives are "sandwich" compounds and stack in a crystal lattice, the addition of bulky groups (such as $CF_3$) could sterically hinder stacking and make these compounds liquids. Availability of fluorinated derivatives is questionable; however, mixed cyclopentadienyl nitrosyl derivatives are known.

4. Sulfur and Sulfur Nitrogen Compounds

Some evidence indicates that sulfur may have a chemical fire suppression activity (Reference 50). $SF_6$ has a very low toxicity, but it has a long atmospheric lifetime. Substituting a bromine atom for a fluorine atom will likely increase the toxicity above that of the parent molecule. Therefore, sulfur compounds in the form $SF_5$-X where X = -$CF_2Br$ or -$CF_2CF_2Br$ group lead the list of sulfur compounds that will be considered. Although $SF_6$ has a long atmospheric lifetime, the presence of the S-C bond in the mentioned materials will lower the lifetime significantly because (1) the bond is weak and (2) the presence of sulfur allows for new reaction mechanisms due to the possibility of valence shell expansion.

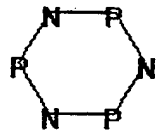
$SF_6$ is a sulfur(VI) compound. Compounds containing sulfur(II) (-S-) and sulfur(IV) (>S<) will also be considered; however, sulfur (II) compounds tend to be more toxic and noxious. In addition a number of sulfur nitrogen compounds exist, and such compounds could prove effective means of delivering sulfur to a fire.

5. Phosphorus Compounds

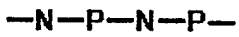
As with silicon compounds, phosphorus-halogen bonds generally confer high toxicity. Phosphorus compounds would have a low atmospheric lifetime because of the weak bonds and the availability of new reaction mechanisms resulting from the expansion of the valence shell. The most likely compounds that could have acceptable toxicities are the phosphazenes (phosphorus nitrides).

Phosphorus nitride compounds include two groups: cyclic compounds containing a cyclic backbone (usually containing alternating phosphorus and nitrogen atoms) and

compounds having a backbone containing linear chains (but which also may contain cyclic substituents along the chain). The latter are often, but not always, 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.



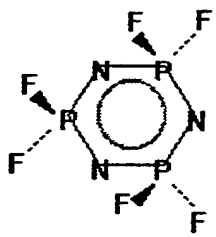
Cyclic

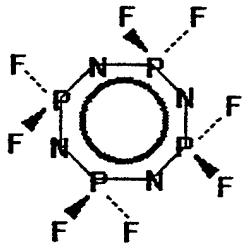



Chain

The backbones may contain substituents including but not limited to the halogens fluorine (F), chlorine (Cl), bromine (Br), and iodine (I); imino groups (=NH); alkyl and substituted alkyl groups; aryl and substituted aryl groups; and alkoxides. Alkyl groups are groups containing only carbon and hydrogen atoms such as methyl ($-CH_3$), ethyl ($-CH_2CH_3$), *n*-propyl ($-CH_2CH_2CH_3$), and *iso*-propyl ($CH(CH_3)_2$). Substituted alkyl groups are alkyl groups in which one or more of the hydrogen (H) atoms have been replaced by other atoms or groups. Examples are $-CH_2F$, $-CHF_2$, and $-CF_3$. Aryl groups are groups containing only carbon and hydrogen atoms in "aromatic" rings. The most common of these is the phenyl group, $-C_6H_5$. Substituted aryl groups have one or more of the hydrogen atoms replaced by some other substituent. An example is perfluorophenyl, $-C_6F_5$. Alkoxide groups have the structure -OR, where R is an alkyl or a substituted alkyl group.

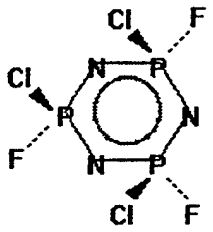
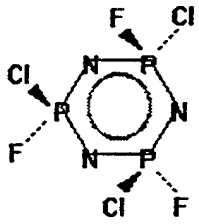
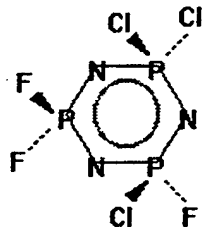
Potential agents include the cyclic phosphorus fluoronitride compounds $P_3N_3F_6$, $P_4N_4F_8$, and, in general, cyclic compounds having a formula $(PNF_2)_n$, where "n" is 2 or greater. These compounds have the cyclic PN backbone with fluorine atoms as substituents. For example, the structures of the "trimer" $P_3N_3F_6$ and "tetramer" $P_4N_4F_8$ are shown below.



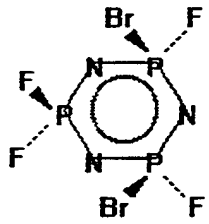


The compounds also include the cyclic phosphorus chloronitride compounds $P_3N_3Cl_6$, $P_4N_4Cl_8$, and, in general, cyclic compounds having a formula $(PNCl_2)_n$, where "n" is 2 or greater. Cyclic phosphorus nitrides containing both fluorine and chlorine in the same molecule are also

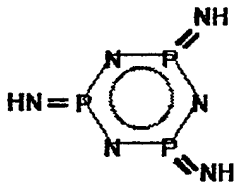
included. Examples of trimers are $P_3N_3ClF_5$, $P_3N_3Cl_2F_4$, $P_3N_3Cl_3F_3$, $P_3N_3Cl_4F_2$, and $P_3N_3Cl_5F$. These include all isomers of the compounds. Isomers are different arrangements of the atoms on the same molecule. For example, three isomers available for $P_3N_3Cl_3F_3$ are shown below.

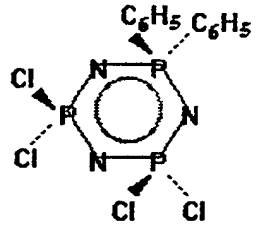
Bromine and iodine substituents may also be present. Cis-2,4-dibromo-2,4,6,6-tetrafluoro-1,3,5,2,4,6-triazaphosphorine is an example of a mixed fluorine/bromine substituted 6-membered ring:



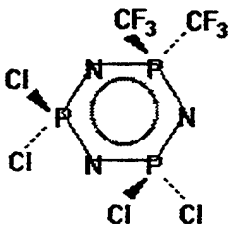
Examples of rings containing imino (=NH), aryl (here, phenyl, $-C_6H_5$), alkyl (here, trifluoromethyl, $-CF_3$), and alkoxy (here, methoxy, $-OCH_3$) are shown below.



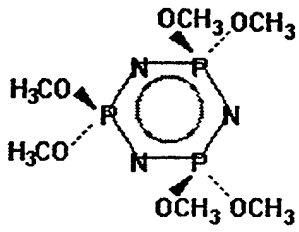
Phospham (Containing Imino Groups)



Containing Phenyl ($-C_6H_5$) Groups



Containing Trifluoromethyl (-CF3) Groups

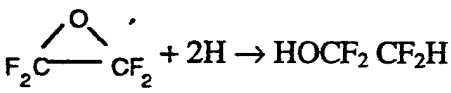


Containing Methoxy (-OCH3) Groups

In addition to cyclic rings, phosphorus/nitrogen compounds also form chains. One example of a simple linear molecule is $Cl_3P=N-PCl_2=NCl$. Phosphorus nitride chain compounds are often polymeric and contain a mixture of chains of different lengths and may also contain some cyclic compounds within the mixture or attached to the chains. For example, when heated above 300°C, phosphorus fluoronitrides form colorless polymeric liquids. The polymeric liquids are believed to contain a mixture of chains of the type $F_3P=N-[PF_2=N]_n-PF_4$, where n is the number of repeating $PF_2=N$ units.

6. Epoxides

Because epoxides are generally highly reactive molecules, it is suggested that they will likely be effective extinguishants, but their reactivity may also lead to high toxicity. The simplest fluorinated epoxide is perfluoroepoxyethane. One proposed fire suppression mechanism is the reaction with hydroxyl free radicals as shown in Reaction [22]. This would be effective both in terms of fire suppression and lowering atmospheric lifetime.




[22]

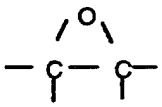
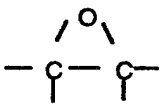
7. Nitrosyl Compounds

Nitrosyl compounds are known to be free radical scavengers, and could, therefore, play a role in removing free radicals that maintain combustion. Although a number of alkyl substituents could be considered, perfluoroalkyls are most likely to have a zero flammability while not adding to agent toxicity. It must be noted, however, that other derivatives could be considered. The simplest perfluorinated nitrosyl compound is $CF_3$-NO. Due to their high reactivity, nitrosyls will undoubtedly have low atmospheric lifetimes.

## B. BROAD LIST OF CANDIDATES

A list of candidates was developed by combining features given in Section IV.A to give chemicals that may have high extinguishing effectiveness along with low atmospheric lifetimes. Making these combinations yield several classes or families of chemicals. These families are listed in Table 3.

TABLE 3. CHEMICAL CLASSES HAVING HIGH FLAME SUPPRESSION CAPABILITIES AND SHORT ATMOSPHERIC LIFETIMES.

| Chemical Family | Features Enhancing Flame Suppression | Features Shortening Atmospheric Lifetime |
|---|---|---|
| Bromoalkenes | Bromine | C = C |
| Brominated aromatics | Bromine | C = C |
| Brominated Ketones, Aldehydes, Esters, Carboxylic Acids | Bromine | –C(O)– |
| Brominated alcohols | Bromine | OH |
| Bromoethers | Bromine | OH |
| Brominated amines, amides, and morpholines | Bromine | Nitrogen |
| Brominated silicon compounds | Bromine | Silicon |
| Fluoroiodocarbons | Iodine | Iodine |
| Metals | Metals | Metals |
| Sulfur and sulfur nitrogen compounds | Sulfur | Sulfur, Nitrogen |
| Phosphonitriles | Phosphorus | Phosphorus |
| Brominated phosphonitriles | Phosphorus, bromine | Phosphorus |
| Epoxides |  |  |
| Nitrosyls | Nitrosyl bonds | Nitrosyl bonds |

Specific chemicals were selected within each of these families by identifying the simplest "parent" molecule and making variations of the parent, which incorporated desirable features that increased the flame suppression capabilities and reduced the atmospheric lifetime. Table 4 shows a list of potential agents under consideration. Other compounds will be added as research continues. This Broad List is intended to be large to allow for later screening of the chemicals on a number of criteria. For some families (i.e., phosphonitriles and sulfur derivatives), non-brominated variations of the parent will not be ruled out until further research indicates that these compounds are not effective fire suppressants.

## C. COLLECTION OR PREDICTION OF INFORMATION ON POTENTIAL AGENTS

Readily available information on physical/chemical properties and toxicity pertaining to the chemicals on this Broad List was collected and compiled. Available information was entered into a Microsoft ACCESS® "COMPDS.MDB" database, which is used to store information on advanced agent candidates. A representative data entry screen within the compound database is provided as Figures 1 and 2. All the information in the database is linked to the citation of the source from which the data were derived. Sources for the information include the open literature, other databases, and industry contacts. The work in Task 2 is designed to address readily available information. Other tasks address issues in more depth and, in some cases, are designed to develop unavailable data. Accordingly, the collection or prediction of information on the Broad List of chemicals encompasses work described in Tasks 3, 4, and 5. Information from these tasks will be used during the final down selection process and will be presented in the final report.

Table 5 presents the physical/chemical property information. These properties were compiled from the literature or from industry contacts. References are contained in the CMPD database.

Several on-line toxicological databases within the National Library of Medicine were searched in an effort to find all toxicity and health effects information on these candidates. The on-line databases searched included the Registry of Toxic Effects of Chemical Substances

TABLE 4. POTENTIAL CANDIDATES FOR THE BROAD LIST.

| IUPAC Name | Formula | CAS Number* |
|---|---|---|
| BROMINATED ALKENES | | |
| 3-Bromo-3,3-difluoropropene | $CH_2$=CHCBr$F_2$ | 420-90-6 |
| 3-(Bromodifluoromethyl)-3,4,4,4-tetrafluorobutene | $CH_2$=CHCF(CBr$F_2$)C$F_3$ | 2546-54-5 |
| 4-Bromo-3,3,4,4-tetrafluorobutene | $CH_2$=CHC$F_2$CBr$F_2$ | 18599-22-9 |
| 2,3-Dibromo-3,3-difluoropropene | $CH_2$=CBrCBr$F_2$ | 677-35-0 |
| 4-Bromo-3-chloro-3,4,4-trifluorobutene | $CH_2$=CHCClFCBr$F_2$ | 374-25-4 |
| 1,2-Dibromo-3,3,3-trifluoropropene | CHBr=CBrC$F_3$ | 431-22-1 |
| 3-Bromo-1,1,3,3-tetrafluoropropene | $CF_2$=CHC$F_2$Br | 460-61-7 |
| 2-Bromo-3,3,3-trifluoropropene | $CH_2$=CBrC$F_3$ | 1514-82-5 |
| 1-Bromo-3,3,3-trifluoropropene | CHBr=CHC$F_3$ | 460-33-3 |
| BROMINATED AROMATICS (Parent = hexafluorobenzene) | | |
| Bromopentafluorobenzene | $C_6$Br$F_5$ | 344-04-7 |
| Bromodifluoromethylpentafluorobenzene | $C_6F_5CF_2$Br | --- |
| BROMINATED KETONES, ALDEHYDES, ESTERS, CARBOXYLIC ACIDS | | |
| Methyl-2-bromo-2,2-difluoroethylketone | $CF_2BrCH_2C(O)CH_3$ | --- |
| 3-Bromo-3,3-difluoropropanaldehyde | $CF_2BrCH_2C(O)H$ | --- |
| 3-Bromo-3,3-difluoropropanoate | $CF_2BrCH_2COOCH_3$ | --- |
| 3-Bromo-3,3-difluoropropanoic acid | $CF_2BrCH_2COOH$ | --- |
| BROMINATED ALCOHOLS | | |
| 2-Bromo-2,2-difluoroethanol | $CF_2BrCH_2OH$ | --- |
| 3-Bromo-3,3-difluoropropanol | $CF_2BrCH_2CH_2OH$ | --- |

* CAS Numbers may be available for some of those chemicals listed without CAS Numbers specified. CAS Number searches are continuing.

TABLE 4. POTENTIAL CANDIDATES FOR THE BROAD LIST (CONTINUED).

| IUPAC Name | Formula | CAS Number* |
|---|---|---|
| BROMINATED ETHERS (Parent = $CF_3OCF_3$) | | |
| Bromodifluoromethyl difluoromethyl ether | $CBrF_2OCHF_2$ | --- |
| Bromodifluoromethyl trifluoromethyl ether | $CBrF_2OCF_3$ | --- |
| 2-Bromo-1,1,2,2-tetrafluoroethyl difluoromethyl ether | $CBrF_2CF_3OCHF_2$ | 32778-13-5 |
| Bromodifluoromethyl methyl ether | $CBrF_2OCH_3$ | --- |
| AMINES (Parent = $N(CF_2)_3$), AMIDES, AND MORPHOLINES | | |
| Tris(bromodifluoromethyl)amine | $N(CF_2Br)_3$ | --- |
| Bis(trifluoromethyl)bromodifluoromethyl amine | $N(CF_3)_2(CF_2Br)$ | --- |
| 3-Bromo-3,3-difluoropropionamide | $CF_2BrCF_2C(O)NH_2$ | --- |
| N-Trifluoromethylbromoheptafluoro-1,4-oxazine | $-OCF_2CFBrN(CF_3)-CF_2CF_2-$ | --- |
| N-Bromodifluoromethyloctafluoro-1,4-oxazine | $-OCF_2CF_2N(CBrF_2)-CF_2CF_2-$ | --- |
| BROMINATED SILICON COMPOUNDS | | |
| Bromodifluoro(trifluorosilyl) methane | $F_3SiCF_2Br$ | --- |
| 1-Bromo-1,1,2,2-tetrafluoro-2-trifluorosilyl ethane | $F_3SiCF_2CF_2Br$ | --- |
| FLUOROIODOCARBONS | | |
| Trifluoroiodomethane | $CF_3I$ | 2314-97-8 |
| Difluoroiodomethane | $CHF_2I$ | 1493-03-4 |
| Fluoroiodomethane | $CH_2FI$ | 373-53-5 |
| Pentafluoroiodoethane | $CF_3CF_2I$ | 354-64-3 |
| Heptafluoro-1-iodopropane | $CF_3CF_2CF_2I$ | 754-34-7 |
| Heptafluoro-2-iodopropane | $CF_3CFICF_3$ | 677-69-0 |

* CAS Numbers may be available for some of those chemicals listed without CAS Numbers specified. CAS Number searches are continuing.

Table 4. POTENTIAL CANDIDATES FOR THE BROAD LIST (CONTINUED).

| IUPAC Name | Formula | CAS Number* |
|---|---|---|
| Nonafluoro-1-iodobutane | $CF_3CF_2CF_2CF_2I$ | 423-39-2 |
| Octafluoro-1,4-diiodobutane | $CF_2ICF_2CF_2CF_2I$ | 375-50-8 |
| Tridecafluoro-1-iodohexane | $CF_3CF_2CF_2CF_2CF_2CF_2I$ | 355-43-1 |
| Heptadecafluoro-1-iodooctane | $CF_3CF_2CF_2CF_2CF_2CF_2CF_2CF_2I$ | 507-63-1 |
| TRANSITION METALS | | |
| Pentacarbonyl(trifluoromethyl) manganese | $Mn(CO)_2CF_3$ | 13601-14-4 |
| Pentacarbonyl(pentafluoroethyl) manganese | $Mn(CO)_5C_2F_5$ | 20791-80-4 |
| Pentacarbonyl(tetrafluoro-1-(trifluoromethyl)ethyl) manganese | $Mn(CO)_5CF(CF_3)_2$ | 127233-81-2 |
| Pentacarbonyl(heptafluoropropyl) manganese | $Mn(CO)_5C_3F_7$ | 93223-74-6 |
| Tetracarbonyl(trifluoromethyl) cobalt | $Ca(CO)_4CF_3$ | 15892-59-8 |
| Tetracarbonyl(pentafluoroethyl) cobalt | $Co(CO)_4C_2F_5$ | 18703-18-9 |
| Tetracarbonyl(tetrafluoro-1-(trifluoromethyl) ethyl) cobalt | $Co(CO)_4CF(CF_2)_2$ | 57306-82-8 |
| Tetracarbonyl(heptafluoropropyl) cobalt | $Co(CO)_4C_3F_7$ | 23254-19-5 |
| Bis(cyclopentadienyl) iron (II) | $Fe(C_5H_5)_2$ | 102-54-5 |
| Diethoxydihydroxy titanium(IV) | $Ti(OC_2H_5)_2(OH)_2$ | 131404-53-0 |
| Butoxytrihydroxy titanium(IV) | $Ti(OC_4H_9)(OH)_3$ | 32857-61-7 |
| Diisoproproxydimethoxy titanium(IV) | $Ti_2(OCH_3)_2(OCHCCH_3)_2$ | 125904-86-1 |
| Dibutoxydihydroxy titanium(IV) | $Ti(OC_4H_9)_2(OH)_2$ | 14531-96-5 |
| Tetramethoxy titanium(IV) | $Ti(OCH_3)_4$ | 992-92-7 |
| Tetraethoxy titanium(IV) | $Ti(OC_2H_5)_4$ | 3087-36-3 |

* CAS Numbers may be available for some of those chemicals listed without CAS Numbers specified. CAS Number searches are continuing.

Table 4. POTENTIAL CANDIDATES FOR THE BROAD LIST (CONTINUED).

| IUPAC Name | Formula | CAS Number* |
|---|---|---|
| NON-TRANSITION METALS | | |
| Bis(Trifluoromethyl) zinc | $Zn(CF_3)_2$ | 70331-87-2 |
| Bromo(trifluoromethyl) zinc | $Br\text{-}Zn\text{-}CF_3$ | 97571-13-6 |
| Chloro(trifluoromethyl) zinc | $Cl\text{-}Zn\text{-}CF_3$ | 97571-14-7 |
| SULFUR HEXAFLUORIDE DERIVATIVES (Parent = $SF_6$) | | |
| Chloropentafluorosulfur(VI) | $SClF_5$ | 13780-57-9 |
| Bromopentafluorosulfur(VI) | $SBrF_5$ | 15607-89-3 |
| Iodopentafluorosulfur(VI) | $SIF_5$ | 65512-39-2 |
| Bis(pentafluorosulfur) oxide | $SF_5OSF_5$ | 42310-84-9 |
| Monokis(bromodifluoro)pentafluorosulfur(VI) | $SF_5CF_2Br$ | — |
| 4,5-Bis(trifluoromethyl)-1,2,3-trithiole | $C_4F_6S_3$ | 142087-13-6 |
| SULFUR NITROGEN COMPOUNDS | | |
| 4,5-Bis(trifluoromethyl)-1,3,2-dithiazol-1-ium | $C_4F_6NS_2$ | 110539-44-1 |
| 4,5-Bis(trifluoromethyl)-1,3,2-dithiazol-2-yl | $C_4F_6NS_2$ | 71042-53-0 |
| 5-(Trifluoromethyl)-1,2,3,4-dithiadiazol-2-yl | $C_2F_3N_2S_2$ | 102860-31-1 |
| 4-(Trifluoromethyl)-1,2,3,5-dithiadiazol-3-yl | $C_2F_3N_2S_2$ | 95095-39-9 |
| NON-BROMINE-CONTAINING PHOSPHONITRILES | | |
| Hexafluoro-1,3,5,2,4,6-triazatriphosphorine | $N_3P_3F_6$ | 15599-91-4 |
| Chloropentafluoro-1,3,5,2,4,6-triazatriphosphorine | $N_3P_3F_5Cl$ | 21846-70-8 |
| 2,2-Dichloro-4,4,6,6-tetrafluoro-1,3,5,2,4,6-triazaphosphorine | $N_3P_3F_4Cl_2$ (gem) | 21846-69-5 |

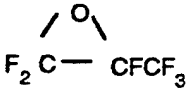
* CAS Numbers may be available for some of those chemicals listed without CAS Numbers specified. CAS Number searches are continuing.

Table 4. POTENTIAL CANDIDATES FOR THE BROAD LIST (CONTINUED).

| IUPAC Name | Formula | CAS Number* |
|---|---|---|
| (cis)-2,4-Dichloro-2,4,6,6-tetrafluoro-1,3,5,2,4,6-triazaphosphorine | $N_3P_3F_4Cl_2$ (cis) | 38589-78-5 |
| (trans)-2,4-Dichloro-2,4,6,6-tetrafluoro-1,3,5,2,4,6-triazaphosphorine | $N_3P_3F_4Cl_2$ (trans) | 38589-82-1 |
| (cis-trans)-2,4,6-Trichloro-2,4,6-trifluoro-1,3,5,2,4,6-triazatriphosphorine | $N_3P_3F_3Cl_3$ (cis-trans) | 38589-80-9 |
| (cis-cis)-2,4,6-Trichloro-2,4,6-trifluoro-1,3,5,2,4,6-triazatriphosphorine | $N_3P_3F_3Cl_3$ (cis-cis) | 38589-79-6 |
| 2,2,4-Trichloro-2,4,6-trifluoro-1,3,5,2,4,6-triazatriphosphorine | $N_3P_3F_3Cl_3$ (gem) | 21846-68-4 |
| (trans)-2,2,4,6-Tetrachloro-4,6-difluoro-1,3,5,2,4,6-triazaphosphorine | $N_3P_3F_2Cl_4$ (trans) | 38589-83-2 |
| (cis)-2,2,4,6-Tetrachloro-4,6-difluoro-1,3,5,2,4,6-triazaphosphorine | $N_3P_3F_2Cl_4$ (cis) | 38589-81-0 |
| 2,2,4,4-Tetrachloro-6,6-difluoro-1,3,5,2,4,6-triazaphosphorine | $N_3P_3F_2Cl_4$ (gem) | 21846-67-3 |
| Pentachlorofluoro-1,3,5,2,4,6-triazaphosphorine | $N_3P_3FCl_5$ | 13778-06-8 |
| Octafluoro-1,3,5,7,2,4,6,8-tetrazatetraphosphorine | $N_4P_4F_8$ | 14700-00-6 |
| Decafluoro-1,3,5,7,9,2,4,6,8,10-pentazapentaphosphorine | $N_5P_5F_{10}$ | 19258-92-5 |
| Dodecafluoro-1,3,5,7,9,11-hexaaza-2,4,6,8,10,12-hexaphosphacyclododecahexene | $N_6P_6F_{12}$ | 19258-93-6 |
| Hexafluoro-1,3-dimethyl-1,2,3,4-diazadiphosphetidine | $C_2H_6F_6N_2P_2$ | 3880-04-4 |
| <u>BROMINATED PHOSPHONITRILES</u> | | |
| Bromopentafluoro-1,3,5,2,4,6-triazaphosphorine | $N_3P_3F_5Br$ | 17022-75-2 |

* CAS Numbers may be available for some of those chemicals listed without CAS Numbers specified. CAS Number searches are continuing.

Table 4. POTENTIAL CANDIDATES FOR THE BROAD LIST (CONCLUDED).

| IUPAC Name | Formula | CAS Number* |
|---|---|---|
| (trans)-2,4-Dibromo-2,4,6,6-tetrafluoro-1,3,5,2,4,6-triazaphosphorine | $N_3P_3F_4Br_2$ (trans) | 38589-73-0 |
| (cis)-2,4-Dibromo-2,4,6,6-tetrafluoro-1,3,5,2,4,6-triaaphosphorine | $N_3P_3F_4Br_2$ (cis) | 38589-72-9 |
| 2,2-Dibromo-4,4,6,6-tetrafluoro-1,3,5,2,4,6-triazaphosphorine | $N_3P_3F_4Br_2$ (gem) | 17022-76-3 |
| (cis-trans)-2,4,6-Tribromo-2,4,6-trifluoro-1,3,5,2,4,6-triazaphosphorine | $N_3P_3F_3Br_3$ (cis-trans) | 38589-75-2 |
| (cis-cis)-2,4,6-Tribromo-2,4,6-trifluoro-1,3,5,2,4,6-triazaphosphorine | $N_3P_3F_3Br_3$ (cis-cis) | 38589-74-1 |
| 2,2,4-Tribromo-4,6,6-trfluoro-1,3,5,2,4,6-triazaphosphorine | $N_3P_3F_3Br_3$ (gem) | 17022-77-4 |
| (trans)-2,2,4,6-Tetrabromo-4,6-difluoro-1,3,5,2,4,6-triazaphosphorine | $N_3P_3F_2Br_4$ (trans) | 38589-77-4 |
| (cis)-2,2,4,6-Tetrabromo-4,6-difluoro-1,3,5,2,4,6-triazaphosphorine | $N_3P_3F_2Br_4$ (cis) | 38589-76-3 |
| 2,2,4,4-Tetrabromo-6,6-difluoro-1,3,5,2,4,6-triazaphosphorine | $N_3P_3F_2Br_4$ (gem) | 17022-78-5 |
| EPOXIDES | | |
| Hexafluoro-1,2-epoxypropane |  | 428-59-1 |
| NITROXIDES | | |
| Bis(trifluoromethyl) nitroxide | $(CF_3)_2NO$ | 2154-71-4 |
| Bis(pentafluoroethyl) nitroxide | $(C_3F_5)_2NO$ | 102259-92-7 |

* CAS Numbers may be available for some of those chemicals listed without CAS Numbers specified. CAS Number searches are continuing.

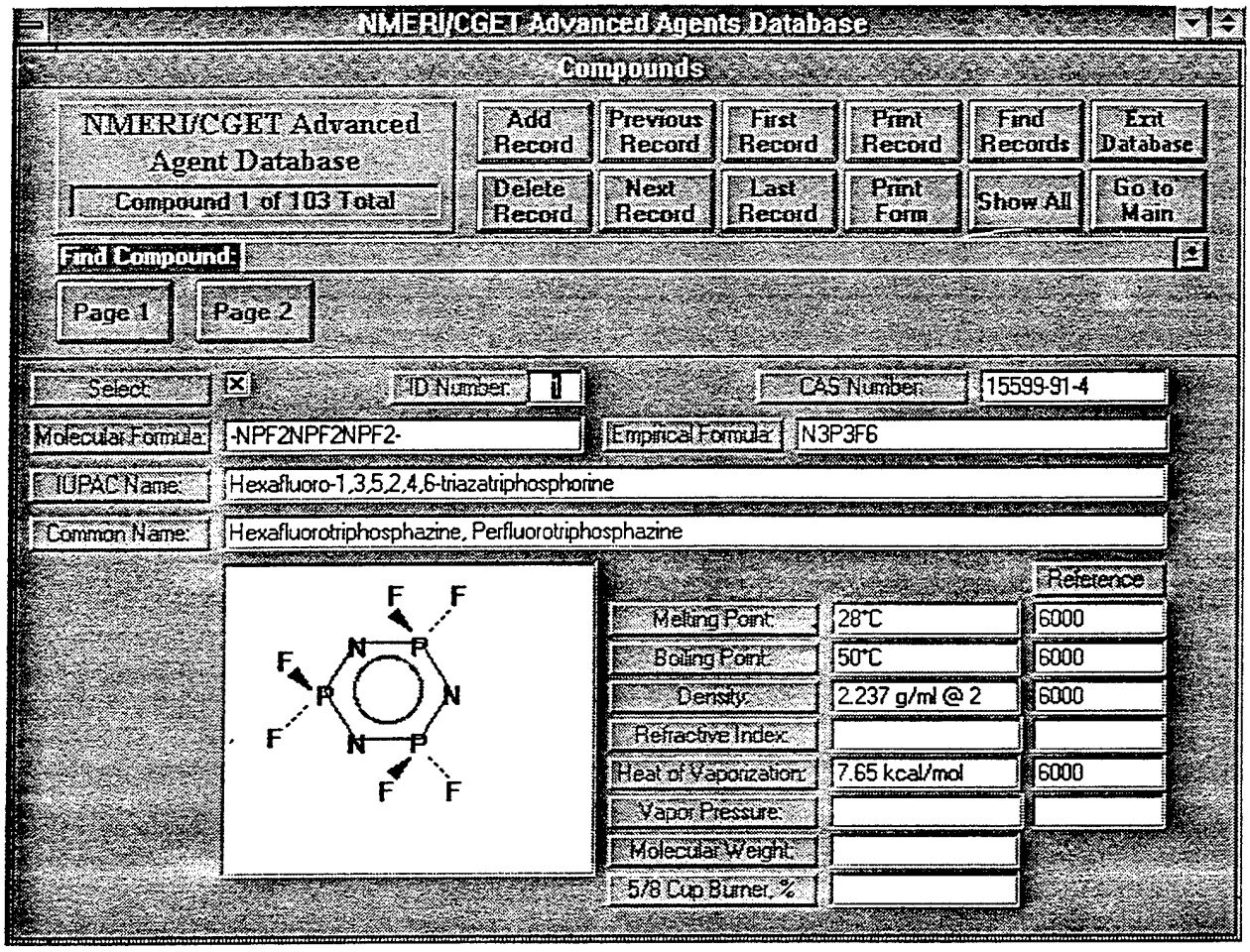



Figure 1. Page 1 of representative data entry screen of compound database.

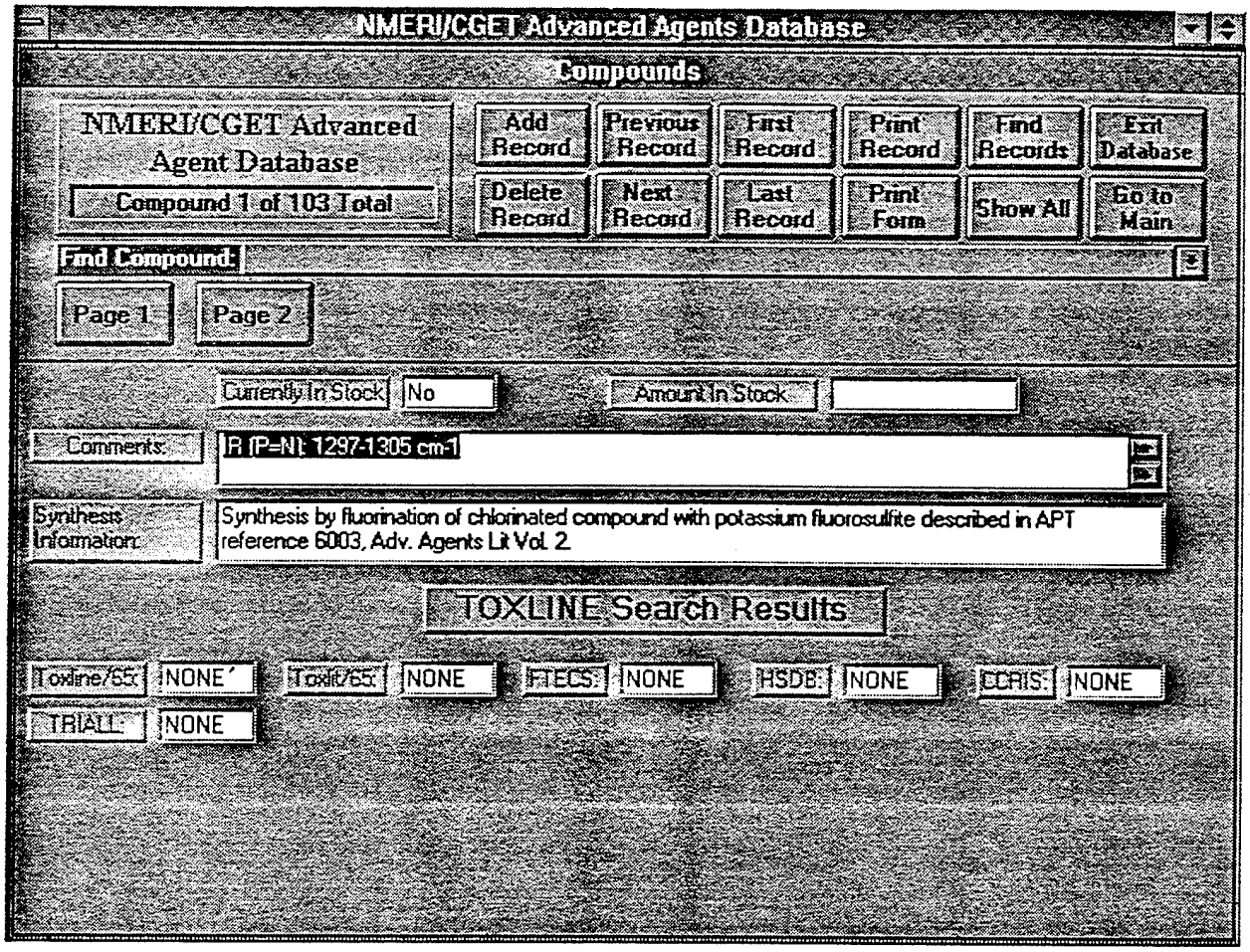



Figure 2. Page 2 of representative data entry screen of compound database.

TABLE 5. PHYSICAL/CHEMICAL PROPERTIES OF THE POTENTIAL CANDIDATES.*

| IUPAC Name | Melting Point, °C | Boiling Point, °C | Density, g/ml | Heat of Vaporization, kcal/mol |
|---|---|---|---|---|
| BROMINATED ALKENES | | | | |
| 3-Bromo-3,3-difluoropropene | ----- | 42 | ----- | ----- |
| 3-(Bromodifluoromethyl)-3,4,4,4-tetrafluorobutene | ----- | 79.5 | 1.67 @ 21 °C | ----- |
| 4-Bromo-3,3,4,4-tetrafluorobutene | ----- | 55 | 1.357 | ----- |
| 2,3-Dibromo-3,3-difluoropropene | ----- | 100 | ----- | ----- |
| 4-Bromo-3-chloro-3,4,4-trifluorobutene | ----- | 99.5 | 1.678 | ----- |
| 1,2-Dibromo-3,3,3-trifluoropropene | ----- | 96 | ----- | ----- |
| 3-Bromo-1,1,3,3-tetrafluoropropene | ----- | 35 | 1.75 | ----- |
| 2-Bromo-3,3,3-trifluoropropene | ----- | 34-35 | 1.69 @ 16 °C | ----- |
| 1-Bromo-3,3,3-trifluoropropene | ----- | 33 | 1.65 | ----- |
| BROMINATED AROMATICS (Parent = hexafluorobenzene) | | | | |
| Bromopentafluorobenzene | ----- | ----- | ----- | ----- |
| Bromodifluoromethylpentafluorobenzene | ----- | ----- | ----- | ----- |
| BROMINATED KETONES, ALDEHYDES, ESTERS, CARBOXYLIC ACIDS | | | | |
| Methyl-2-bromo-2,2-difluoroethylketone | ----- | ----- | ----- | ----- |
| 3-Bromo-3,3-difluoropropanaldehyde | ----- | ----- | ----- | ----- |

* Physical properties for chemicals listed have not been found and may not exist.

TABLE 5. PHYSICAL/CHEMICAL PROPERTIES OF THE POTENTIAL CANDIDATES (CONTINUED).*

| IUPAC Name | Melting Point, °C | Boiling Point, °C | Density, g/ml | Heat of Vaporization, kcal/mol |
|---|---|---|---|---|
| 3-Bromo-3,3-difluoropropanoate | ----- | ----- | ----- | ----- |
| 3-Bromo-3,3-difluoropropanoic acid | ----- | ----- | ----- | ----- |
| BROMINATED ALCOHOLS | | | | |
| 2-Bromo-2,2-difluoroethanol | ----- | ----- | ----- | ----- |
| 3-Bromo-3,3-difluoropropanol | ----- | ----- | ----- | ----- |
| BROMINATED ETHERS (Parent = $CF_3OCF_3$) | | | | |
| Bromodifluoromethyl difluoromethyl ether | ----- | 24.6 | ----- | ----- |
| Bromodifluoromethyl trifluoromethyl ether | ----- | -5.4 | ----- | ----- |
| 2-Bromo-1,1,2,2-tetrafluoroethyl difluoromethyl ether | ----- | 45 | ----- | ----- |
| Bromodifluoromethyl methyl ether | ----- | ----- | ----- | ----- |
| AMINES (Parent = $N(CF_3)_3$), AMIDES, AND MORPHOLINES | | | | |
| Tris(bromodifluoromethyl)amine | ----- | ----- | ----- | ----- |
| Bis(trifluoromethyl)bromodifluoromethyl amine | ----- | ----- | ----- | ----- |
| 3-Bromo-3,3-difluoropropionamide | ----- | ----- | ----- | ----- |
| N-Trifluoromethylbromoheptafluoro-1,4-oxazine | ----- | ----- | ----- | ----- |
| N-Bromodifluoromethyloctafluoro-1,4-oxazine | ----- | ----- | ----- | ----- |
| BROMINATED SILICON COMPOUNDS | ----- | ----- | ----- | ----- |
| Bromodifluoro(trifluorosilyl) methane | ----- | ----- | ----- | ----- |
| 1-Bromo-1,1,2,2-tetrafluoro-2-trifluorosilyl ethane | ----- | ----- | ----- | ----- |

* Physical properties for chemicals listed have not been found and may not exist.

TABLE 5. PHYSICAL/CHEMICAL PROPERTIES OF THE POTENTIAL CANDIDATES (CONTINUED).*

| IUPAC Name | Melting Point, °C | Boiling Point, °C | Density, g/ml | Heat of Vaporization kcal/mol |
|---|---|---|---|---|
| FLUOROIODOCARBONS | | | | |
| Trifluoroiodomethane | ----- | -22.5 | 2.096 @ 25 °C | 22.41 kJ/mol |
| Difluoroiodomethane | -122 | 21.6 | 3.238 @ -19 °C | 25.99 kJ/mol |
| Fluoroiodomethane | ----- | 53.4 | 2.366 @ 20 °C | ----- |
| Pentafluoroiodoethane | ----- | 13 | 2.07 | ----- |
| Heptafluoro-1-iodopropane | -95.3 | 41 | 2.06 | ----- |
| Heptafluoro-2-iodopropane | ----- | 40 | 2.099 @ 20 °C | ----- |
| Nonafluoro-1-iodobutane | ----- | ----- | 2.01 | ----- |
| Octafluoro-1,4-diiodobutane | ----- | 85 | 2.50 | ----- |
| Tridecafluoro-1-iodohexane | ----- | 117 | 2.05 @ 20 °C | ----- |
| Heptadecafluoro-1-iodooctane | ----- | 160.5 | 2.04 | ----- |
| TRANSITION METALS | | | | |
| Pentacarbonyl(trifluoromethyl) manganese | 82-83 | 70 @ 20 mm (subl.) | ----- | ----- |
| Pentacarbonyl(pentafluoroethyl) manganese | ----- | ----- | ----- | ----- |
| Pentacarbonyl(tetrafluoro-1-(trifluoromethyl)ethyl) manganese | 2 | 73 @ 17 mm | ----- | ----- |

* Physical properties for chemicals listed have not been found and may not exist.

TABLE 5. PHYSICAL/CHEMICAL PROPERTIES OF THE POTENTIAL CANDIDATES (CONTINUED).*

| IUPAC Name | Melting Point, °C | Boiling Point, °C | Density, g/ml | Heat of Vaporization, kcal/mol |
|---|---|---|---|---|
| Pentacarbonyl(heptafluoropropyl) manganese | ----- | 56 @ 3 mm | ----- | ----- |
| Tetracarbonyl(trifluoromethyl) cobalt | 10.5-11 | 31 @ 28 mm -91 @ 760 mm | ----- | ----- |
| Tetracarbonyl(pentafluoroethyl) cobalt | ----- | 32 @ 16 mm, -110 @ 760 mm | ----- | ----- |
| Tetracarbonyl(tetrafluoro-1-(trifluoromethyl) ethyl) cobalt | ----- | ----- | ----- | ----- |
| Tetracarbonyl(heptafluoropropyl) cobalt | ----- | 44 @ 16 mm | ----- | ----- |
| Bis(cyclopentadienyl) iron (II) | 175-249 | ----- | ----- | ----- |
| Diethoxydihydroxy titanium(IV) | ----- | ----- | ----- | ----- |
| Butoxytrihydroxy titanium(IV) | ----- | ----- | ----- | ----- |
| Diisopropyloxydimethoxy titanium(IV) | ----- | ----- | ----- | ----- |
| Dibutoxydihydroxy titanium(IV) | ----- | ----- | ----- | ----- |
| Tetramethoxy titanium(IV) | ----- | ----- | ----- | ----- |
| Tetraethoxy titanium(IV) | ----- | ----- | ----- | ----- |
| NON-TRANSITION METALS | ----- | ----- | ----- | ----- |
| Bis(Trifluoromethyl) zinc | ----- | ----- | ----- | ----- |
| Bromo(trifluoromethyl) zinc | ----- | ----- | ----- | ----- |
| Chloro(trifluoromethyl) zinc | ----- | ----- | ----- | ----- |

* Physical properties for chemicals listed have not been found and may not exist.

TABLE 5. PHYSICAL/CHEMICAL PROPERTIES OF THE POTENTIAL CANDIDATES (CONTINUED).*

| IUPAC Name | Melting Point, °C | Boiling Point, °C | Density, g/ml | Heat of Vaporization, kcal/mol |
|---|---|---|---|---|
| SULFUR HEXAFLUORIDE DERIVATIVES (Parent = $SF_6$) | | | | |
| Chloropentafluorosulfur(VI) | ----- | ----- | ----- | ----- |
| Bromopentafluorosulfur(VI) | ----- | ----- | ----- | ----- |
| Iodopentafluorosulfur(VI) | ----- | ----- | ----- | ----- |
| Bis(pentafluorosulfur) oxide | ----- | ----- | ----- | ----- |
| Monokis(bromodifluoro)pentafluorosulfur(VI) | ----- | ----- | ----- | ----- |
| 4,5-Bis(trifluoromethyl)-1,2,3-trithiole | ----- | ----- | ----- | ----- |
| SULFUR NITROGEN COMPOUNDS | | | | |
| 4,5-bis(Trifluoromethyl)-1,3,2-dithiazol-1-ium | ----- | ----- | ----- | ----- |
| 4,5-bis(Trifluoromethyl)-1,3,2-dithiazol-2-yl | 12 | 119 (extrapolated) | ----- | ----- |
| 5-(Trifluoromethyl)-1,2,3,4-dithiadiazol-2-yl | ----- | ----- | ----- | ----- |
| 4-(Trifluoromethyl)-3H-1,2,3,5-Dithiadiazol-3-yl | ----- | ----- | ----- | ----- |
| NON-BROMINE-CONTAINING PHOSPHONITRILES | | | | |
| Hexafluoro-1,3,5,2,4,6-triazatriphosphorine | 28 | 50 | 2.237 | 7 |
| Chloropentafluoro-1,3,5,2,4,6-triazatriphosphorine | -30 | 81 | 1.759 | 8 |
| 2,2-Dichloro-4,4,6,6-tetrafluoro-1,3,5,2,4,6-triazaphosphorine | -46 | 114.7 | 1.765 | 9.6 |
| (cis)-2,4-Dichloro-2,4,6,6-tetrafluoro-1,3,5,2,4,6-triazaphosphorine | ----- | 140 | ----- | ----- |

* Physical properties for chemicals listed have not been found and may not exist.

TABLE 5. PHYSICAL/CHEMICAL PROPERTIES OF THE POTENTIAL CANDIDATES (CONTINUED).*

| IUPAC Name | Melting Point, °C | Boiling Point, °C | Density, g/ml | Heat of Vaporization, kcal/mol |
|---|---|---|---|---|
| (trans)-2,4-Dichloro-2,4,6,6-tetrafluoro-1,3,5,2,4,6-triazaphosphorine | ----- | 140 | ----- | ----- |
| (cis-trans)-2,4,6-Trichloro-2,4,6-trifluoro-1,3,5,2,4,6-triazatriphosphorine | ----- | ----- | ----- | ----- |
| (cis-cis)-2,4,6-Trichloro-2,4,6-trifluoro-1,3,5,2,4,6-triazatriphosphorine | ----- | ----- | ----- | ----- |
| 2,2,4-Trichloro-2,4,6-trifluoro-1,3,5,2,4,6-triazatriphosphorine | -35 | 150 | 1.759 | 10.2 |
| (trans)-2,2,4,6-Tetrachloro-4,6-difluoro-1,3,5,2,4,6-triazaphosphorine | ----- | 170 | ----- | ----- |
| (cis)-2,2,4,6-Tetrachloro-4,6-difluoro-1,3,5,2,4,6-triazaphosphorine | ----- | 170 | ----- | ----- |
| 2,2,4,4-Tetrachloro-6,6-difluoro-1,3,5,2,4,6-triazaphosphorine | 18 | 181.6 | 1.785 | 11.0 |
| Pentachlorofluoro-1,3,5,2,4,6-triazaphosphorine | 50 | 215 | 1.981 | 12.5 |
| Octafluoro-1,3,5,7,2,4,6,8-tetrazatetraphosphocine | 30.4 | 89.7 | 2.239 | 8.91 |
| Decafluoro-1,3,5,7,9,2,4,6,8,10-pentazapentaphosphecine | -50 | 120.1 | 1.826 | 9.80 |
| Dodecafluoro-1,3,5,7,9,11-hexaaza-2,4,6,8,10,12-hexaphosphacyclododecahexene | -45.5 | 147.2 | 1.841 | ----- |
| Hexafluoro-1,3-dimethyl-1,2,3,4-diazadiphosphetidine | -8.3 to -10.3 | 91.6 @ 757 mm | 1.532 | ----- |

* Physical properties for chemicals listed have not been found and may not exist.

TABLE 5. PHYSICAL/CHEMICAL PROPERTIES OF THE POTENTIAL CANDIDATES (CONTINUED).*

| IUPAC Name | Melting Point, °C | Boiling Point, °C | Density, g/ml | Heat of Vaporization, kcal/mol |
|---|---|---|---|---|
| BROMINATED PHOSPHONITRILES | | | | |
| Bromopentafluoro-1,3,5,2,4,6-triazaphosphorine | ----- | 97 | ----- | ----- |
| (trans)-2,4-Dibromo-2,4,6,6-tetrafluoro-1,3,5,2,4,6-triazaphosphorine | ----- | ----- | ----- | ----- |
| (cis)-2,4-Dibromo-2,4,6,6-tetrafluoro-1,3,5,2,4,6-triaaphosphorine | ----- | ----- | ----- | ----- |
| 2,2-Dibromo-4,4,6,6-tetrafluoro-1,3,5,2,4,6-triazaphosphorine | ----- | ----- | ----- | ----- |
| (cis-trans)-2,4,6-Tribromo-2,4,6-trifluoro-1,3,5,2,4,6-triazaphosphorine | ----- | ----- | ----- | ----- |
| (cis-cis)-2,4,6-Tribromo-2,4,6-trifluoro-1,3,5,2,4,6-triazaphosphorine | ----- | ----- | ----- | ----- |
| 2,2,4-Tribromo-4,6,6-trifluoro-1,3,5,2,4,6-triazaphosphorine | ----- | ----- | ----- | ----- |
| (trans)-2,2,4,6-Tetrabromo-4,6-difluoro-1,3,5,2,4,6-triazaphosphorine | ----- | ----- | ----- | ----- |
| (cis)-2,2,4,6-Tetrabromo-4,6-difluoro-1,3,5,2,4,6-triazaphosphorine | ----- | ----- | ----- | ----- |
| 2,2,4,4-Tetrabromo-6,6-difluoro-1,3,5,2,4,6-triazaphosphorine | ----- | ----- | ----- | ----- |
| EPOXIDES | | | | |
| Hexafluoro-1,2-epoxypropane | ----- | -42 | ----- | ----- |

* Physical properties for chemicals listed have not been found and may not exist.

TABLE 5. PHYSICAL/CHEMICAL PROPERTIES OF THE POTENTIAL CANDIDATES (CONCLUDED).*

| IUPAC Name | Melting Point, °C | Boiling Point, °C | Density, g/ml | Heat of Vaporization, kcal/mol |
|---|---|---|---|---|
| NITROXIDES | | | | |
| Bis(trifluoromethyl) nitroxide | -70 | -25 | ----- | ----- |
| Bis(pentafluoroethyl) nitroxide | ----- | ----- | ----- | ----- |

* Physical properties for chemicals listed have not been found and may not exist.

(RTECS), Hazardous Substance Data Bank (HSDB), Chemical Carcinogenesis Research Information System (CCRIS), Toxic Chemical Release Inventory (TCRI), Toxline, Toxlit, and Chemical Abstract Service (CAS) Toxicology Section. Initial on-line searches were performed using CAS numbers as the search criteria. For most of the chemicals, no toxicological information was found. For other candidates, several "hits" or records were identified. When information was not found using CAS numbers, generic family names were used as search terms to identify information on other chemicals in the same family as the candidates being searched.

## D. DEVELOPMENT OF WEIGHTED ATTRIBUTES CANDIDATE ASSESSMENT MATRIX

A WACAM approach was originally to be used to select the candidates from the Broad List of chemicals to be considered in more detail. However, after compiling the readily available information on the Broad List candidates, it was determined that an insufficient amount of information existed on most of the candidates to perform a down selection through the WACAM process. In most cases, the fire-extinguishing ability was unknown and needed to be determined for a representative compound from the chemical class before down selection could occur. Therefore, the WACAM will be delayed until later in the project when flame extinguishing data have been determined for selected candidates in several chemical families.

## E. SELECTION OF CANDIDATES FROM EACH FAMILY

Based on availability, a representative candidate or two was or will be selected from each chemical family. Table 6 lists the candidates already selected. This list of representative candidates will be added to as research continues or as compounds from the candidate families become available. The candidates will be tested in the laboratory cup burner to determine the extinguishing efficiency representative of the family. This list will be subject to revision as (1) test data are obtained, (2) regulatory, safety, and environmental issues become better defined, (3) assessments of compounds and chemical families are made, and (4) other candidate compounds or families are identified.

TABLE 6. SELECTED CANDIDATES FOR INITIAL LABORATORY TESTING.

| Name | Formula | Phase | CAS No. | Boiling Pt, °C |
|---|---|---|---|---|
| 3-Bromo-3,3-difluoropropene | $CH_2=CHCF_2Br$ | Liquid | 420-90-6 | 42.0 |
| 2-Bromo-3,3,3-trifluoropropene | $CH_2=CBrCF_3$ | Liquid | 1514-82-5 | 34 |
| Bromopentafluorobenzene | $C_6BrF$ | Liquid | 344-04-7 | 137 |
| Trifluoroiodomethane | $CF_3I$ | Gas | 2314-97-8 | -23 |
| Heptafluoro-1-iodopropane | $C_3F_7I$ | Liquid | 754-34-7 | 41 |
| Heptadecafluoro-1-iodooctane | $C_8F_{17}I$ | Liquid | 507-63-1 | 160.5 |
| Octafluoro-1,4-diiodobutane | $CF_2ICF_2CF_2\ CF_2I$ | Liquid | 375-50-8 | 85 |
| Bis(cyclopentadienyl)iron II | $Fe(C_5H_5)_2$ | Solid | 102-54-5 | 249 |
| Hexafluoro-1,3,5,2,4,6-triazatriphosphorine* | $N_3P_3F_6$ | Liquid | — | — |
| Hexafluoro-1,2,2-epoxypropane | $C_3F_6O$ | Gas | 428-59-1 | — |
| Bis(trifluoromethyl)nitroxide | $(CF_3)_2NO$ | Gas | 2154-71-4 | -25 |

* Also contains various quantities of $N_3P_3F_5Cl$, $N_3P_3F_4Cl_2$, and $N_3P_3F_3Cl_3$.

# SECTION V

# CONCLUSIONS AND RECOMMENDATIONS

## A. CONCLUSIONS

The completed fire-suppression mechanism survey revealed that a number of classes of chemicals hold promise as fire-extinguishing agents. Several of these classes of chemicals extinguish flames by mechanisms other than hydrogen radical scavenging, which is the predominant mechanism in halon fire extinguishment.

An important step in selecting advanced streaming agent candidates is the establishment of selection criteria against which compounds will be compared to determine their appropriateness as streaming agents. In this effort, a list of selection criteria was established and targets were set for each of the parameters. Although these criteria are not stringent determiners of which candidates will be selected, they provide guidelines when making such selections.

The chemical families identified during the candidate survey include brominated alkenes, aromatics, ketones, aldehydes, esters, carboxylic acids, alcohols, ethers, amines, amides, morpholines, and silicon compounds as well as fluoroiodocarbons, metallics, sulfur and sulfur nitrogen compounds, phosphonitriles, epoxides, and nitrosyl compounds. A representative compound from each chemical class has been or will be selected based on availability to test in the laboratory cup burner to determine the flame extinction efficiency of the chemical class. Collection of information will continue on the Broad List of candidates, and in some cases, prediction on properties will be attempted when necessary.

## B. RECOMMENDATIONS

In addition, it is recommended that the issues relating to cleanliness of candidates agents be clarified, since some of the chemical classes (e.g., metals and silicon compounds) identified may leave minimal or significant residue upon discharge from an extinguisher or during interaction with a fire. Depending on the chemical nature of the residue, cleanliness may not cause a problem under typical use, but further work is needed to resolve this question. Finally, issues relating to toxicity of agents should be defined. Definitive studies specifying toxicity criteria should be performed to determine the level of toxicity that is acceptable in typical use scenarios.

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