



# Project Summary

## Low Ozone-Depleting Halocarbons As Total-Flood Agents: Volume 1—Candidate Survey

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**Adequate protection of enclosed facilities against explosions and fires involving flammable gases or streaming liquid fuels poses major safety challenges for the Alaskan North Slope petroleum industry. At present, such facilities are protected by Halon 1301 total-flood fire suppression systems. However, because of its impact on stratospheric ozone, the production of Halon 1301 was halted under international regulation on December 31, 1993. The report describes the results of a survey of possible low ozone-depleting halocarbon replacements for Halon 1301 in North Slope applications. Candidate agents surveyed in this project included perfluorocarbons, hydrofluorocarbons, and hydrochlorofluorocarbons as well as selected hydrobromofluorocarbons, fluoroiodocarbons, haloethers, and haloalkenes. Selection criteria used to evaluate these candidates were physical properties, chemical stability, toxicity, availability, cost, materials compatibility, cleanliness, environmental considerations, and regulatory concerns. Based on these criteria, 29 chemicals are recommended for laboratory-scale testing.**

***This Project Summary was developed by EPA's National Risk Assessment Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).***

### Introduction

Adequate protection of enclosed facilities against explosions and fires involving flammable gases or streaming liquid fuels poses major safety challenges for the Alaskan North Slope petroleum industry. Facilities on the North Slope are presently protected by Halon 1301 total-flood fire suppression systems. However, the cessation of production of Halon 1301 as mandated by the Montreal Protocol for Protection of the Ozone Layer is expected to severely limit future availability of this chemical. The report describes the initial effort undertaken to evaluate other families of halocarbons as substitute total-flood fire and explosion protection agents for North Slope petroleum production, handling, and transport facilities.

The effort was divided into two areas of emphasis: (1) physical action agents (PAAs) and (2) chemical action agents (CAAs). PAAs are chemicals that extinguish fires by a variety of mechanisms including vapor-phase heat absorption, liquid-phase heat absorption, evaporative cooling, thermal dissociation, dilution of fuel and oxygen, and separation of fuel and oxygen. CAAs cause fire extinguishment primarily by removal of free radicals that promote combustion chain reaction mechanisms. For halocarbon agents, significant free radical removal requires the presence of bromine or iodine in the halocarbon. In general, CAAs have higher explosion protection and fire suppression capabilities than PAAs. However, CAAs

also tend to have higher toxicities, and bromine-containing CAAs tend to have high ozone depletion potentials. Assignment of a chemical to either the PAA or CAA category does not imply that the particular agent does not operate by both mechanisms, rather that one action appears to be the predominant mode of extinguishment.

### **Selection of Candidates for Laboratory-Scale Testing**

Available information on the physical properties, chemical stabilities, toxicities, availabilities, costs, materials compatibilities, fire suppression capabilities, and environmental considerations for approximately 650 halogenated hydrocarbons was collected and screened. Sources for the information included the open literature and industry contacts. The effectiveness of an explosion or fire suppression agent depends upon agent deliverability, heat removal capability, and free radical reaction termination capability. Physical properties to be considered when determining the potential of a chemical for total-flood applications include boiling point, freezing point, vapor heat capacity, heat of vaporization, vapor pressure at room temperature, heat of reaction to form products, viscosity, and vapor and liquid density. Some of these properties relate primarily to deliverability (e.g., boiling point, vapor density, viscosity, and vapor pressure) and some to extinguishing ability (e.g., vapor heat capacity and heat of vaporization).

Halon 1301 has a boiling point of  $-58^{\circ}\text{C}$  and is delivered as a gas in fire suppression and explosion prevention applications. For purposes of this initial screening of Halon 1301 alternatives, compounds having known boiling points between  $-150^{\circ}\text{C}$  and  $0^{\circ}\text{C}$  were considered acceptable. When boiling points were not known, an algorithm was used to predict these values and the acceptable range was extended to be  $-170^{\circ}\text{C}$  to  $+20^{\circ}\text{C}$  to allow for error in the predicted values. A preliminary database survey identified 52 PAAs and 40 CAAs with boiling points within the desired boiling point range.

For effective heat removal, an agent should have a high vapor heat capacity and high heat of vaporization. Ideally, the vapor heat capacity and heat of vaporization should be equal to or higher than those of existing agents. However, for this screening no agents were strictly disqualified if they did not meet these criteria. The freezing point of the agent should preferably be below  $-60^{\circ}\text{C}$ . In normal usage an agent would not experience temperatures

below  $0^{\circ}\text{C}$ ; however, cylinders of agent being transported outdoors in wintertime at the Alaskan North Slope could be exposed to temperatures as low as  $-60^{\circ}\text{C}$ . Of the 92 chemicals found to have boiling points within the desired boiling point range, all had known freezing points above  $-60^{\circ}\text{C}$ .

Since agents are often stored for long periods before use, sometimes under extremes of temperature, agents must be chemically stable during long-term storage. Chemical stability implies the absence of easy decomposition pathways. Highly fluorinated chemicals are less likely to undergo the oxidative reactions that often destroy molecules containing carbon-to-carbon bonds. During initial screening, agents containing particularly weak carbon-to-halogen bonds were ranked lower than comparable agents with stronger bonds. None of the compounds in the preliminary list of 92 contained any particularly unstable functional groups. Therefore, chemical instability is not expected to be a problem for any of the chemicals.

It is desirable that an alternative agent be as nontoxic as possible. This is especially the case where the agent is to be dispersed as a gas into a room occupied by humans. Exposure of personnel to agents can occur during manufacturing, handling, system maintenance and storage, as well as during agent discharge for fire suppression or explosion prevention. Human and animal studies indicate several possible adverse effects of halocarbons. First, halocarbons can stimulate or suppress the central nervous system to produce symptoms ranging from lethargy and unconsciousness to convulsions and tremors. Second, halocarbons can cause cardiac arrhythmias and can sensitize the heart to epinephrine (adrenaline). Third, inhalation of these chemicals can produce bronchioconstriction, reduce pulmonary compliance, depress respiratory volume, reduce mean arterial blood pressure, and produce tachycardia (rapid heartbeat). Fourth, these agents can cause organ damage by degradation products of metabolism. Lastly, halocarbons can produce cancerous or mutagenic effects. Generalization of toxic effects to an entire class of chemicals is not possible, and toxicity information on each candidate must be individually acquired in order to assess fully its potential health hazards.

For this study, all publicly available toxicity information on the chemicals of interest was collected and evaluated. This was accomplished by performing on-line computer searches of toxicological databases such as Toxlit, Toxline, and Chemical Ab-

stract Services, by manual searches, and in certain circumstances by soliciting unpublished information from industry sources. For many chemicals, little, if any, toxicological information was found. For such chemicals, toxicities were assessed through quantitative structure-activity relationships to achieve preliminary estimates of anesthetic potential and lethal index.

Agent cleanliness is another important consideration for certain applications. Cleanliness is defined as the ability of the fire extinguishant to evaporate rapidly without leaving residue harmful to electronic or other equipment. One of the major advantages of the halons is their cleanliness. They can be used on electronic, electrical, or complex mechanical equipment without requiring subsequent cleanup or causing equipment malfunction. All halocarbons with boiling points below  $50^{\circ}\text{C}$  that do not contain high boiling impurities are expected to be clean. Meeting the cleanliness requirement is not expected to be a problem for any of the agents considered in this study.

Data on ozone depletion potentials (ODPs), global warming potentials (GWPs), and atmospheric lifetimes were collected or estimated. Both ODPs and GWPs depend in part on atmospheric lifetimes. For ODP, a longer lifetime means that a greater proportion of the molecules released reaches the stratosphere where photolysis creates the chlorine or bromine radicals that catalyze destruction of ozone. With respect to global warming, a longer lifetime means that the molecules are absorbing infrared radiation from the surface of the earth and transforming it to kinetic energy for a longer time, resulting in increased warming. Therefore, it is desirable that alternative agents have short atmospheric lifetimes.

### **Conclusions**

Taking all of the available and estimated data together, the 92 chemicals initially selected on the basis of appropriate boiling points were prioritized for further evaluation. Table 1 lists 43 of the 52 PAAs by groups with regard to the desirability for further testing and evaluation. Group 1 PAAs are those which are believed to warrant testing in the laboratory. All of these chemicals have attractive physical properties, potentially low toxicities, acceptable environmental characteristics, and are available for testing. Of these chemicals, all have been tested in a laboratory cup burner apparatus and found to exhibit extinguishing concentrations ranging from 6 to 12% by volume. Group 2 PAAs have attractive physical properties, predicted

**Table 1. Candidate Group List of Physical Action Agents**

Group	Halocarbon Number	Formula	Comment
1 Recommended for Lab-testing	14	CF <sub>4</sub>	toxicity expected to be low
	22	CHClF <sub>2</sub>	low toxicity
	23	CHF <sub>3</sub>	long atmospheric lifetime
	32	CH <sub>2</sub> F <sub>2</sub>	flammable
	116	CF <sub>3</sub> CF <sub>3</sub>	low toxicity
	124	CHClCF <sub>3</sub>	low toxicity
	125	CHF <sub>2</sub> CF <sub>3</sub>	limited availability
	134a	CH <sub>2</sub> FCF <sub>3</sub>	low toxicity
	142b	CClF <sub>2</sub> CH <sub>3</sub>	flammable
	143a	CH <sub>3</sub> CF <sub>3</sub>	flammable
	152a	CHF <sub>2</sub> CH <sub>3</sub>	very low toxicity
	218	CF <sub>3</sub> CF <sub>2</sub> CF <sub>3</sub>	low toxicity
	3-1-10	C <sub>4</sub> F <sub>10</sub>	toxicity expected to be low
	C318	C <sub>4</sub> F <sub>8</sub>	decomposition products may be toxic
2 Recommended for Lab-testing	124a	CHF <sub>2</sub> CClF <sub>2</sub>	unknown tox but expected to be low
	134	CHF <sub>2</sub> CHF <sub>2</sub>	unknown tox but expected to be low
	227ea	CF <sub>3</sub> CHFCF <sub>3</sub>	unknown tox but expected to be low
	236fa	CF <sub>3</sub> CH <sub>2</sub> CF <sub>3</sub>	acute toxicity known
	245cb	CF <sub>3</sub> CF <sub>2</sub> CH <sub>3</sub>	unknown tox but expected to be low
3 Unavailable Commercially	142a	CHClFCH <sub>2</sub> F	no data
	216	CF <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub>	no data
	226ba	CF <sub>3</sub> CClFCHF <sub>2</sub>	no data
	227ca	CF <sub>3</sub> CF <sub>2</sub> CF <sub>2</sub> H	acute toxicity known
	234	CF <sub>2</sub> CF <sub>2</sub> CH <sub>2</sub>	no data
	235cc	CH <sub>2</sub> FCF <sub>2</sub> CClF <sub>2</sub>	acute toxicity known
	235da	CF <sub>3</sub> CHClCHF <sub>2</sub>	anesthetic at low concentrations
	235ca	CHF <sub>2</sub> CF <sub>2</sub> CHClF	anesthetic at low concentrations
	236cb	CH <sub>2</sub> FCF <sub>2</sub> CF <sub>3</sub>	no data
	244db	CF <sub>3</sub> CHClCH <sub>2</sub> F	no data
	244bb	CF <sub>3</sub> CClFCH <sub>3</sub>	anesthetic at low concentrations
	244ca	CHF <sub>2</sub> CF <sub>2</sub> CH <sub>2</sub> Cl	no data
	244fb	CClF <sub>2</sub> CH <sub>2</sub> CHF <sub>2</sub>	acute toxicity known
	244cb	CH <sub>2</sub> FCF <sub>2</sub> CHClF	no data
	244da	CHF <sub>2</sub> CHClCHF <sub>2</sub>	anesthetic at low concentrations
	245eb	CF <sub>3</sub> CHFCH <sub>2</sub> F	no data
	245ea	CHF <sub>2</sub> CHFCHF <sub>2</sub>	no data
	245ca	CHF <sub>2</sub> CHF <sub>2</sub> CH <sub>2</sub> F	no data
	254eb	CF <sub>3</sub> CHFCH <sub>3</sub>	probably flammable, no data
254ea	CHF <sub>2</sub> CHFCH <sub>2</sub> F	probably flammable, no data	
254fa	CHF <sub>2</sub> CH <sub>2</sub> CHF <sub>2</sub>	probably flammable, no data	
254ca	CH <sub>2</sub> CF <sub>2</sub> CH <sub>2</sub> F	probably flammable, no data	
254cb	CHF <sub>2</sub> CF <sub>2</sub> CH <sub>3</sub>	probably flammable, no data	
4 Unacceptable	31	CH <sub>2</sub> ClF	cancer-causing in lab animals

flame extinguishment concentrations ranging between 8 and 11%, and are commercially available. Group 3 chemicals are generally not available; however, several from this group look attractive. For example, HFC-227ca appears to have a relatively low toxicity based on limited acute data, its boiling and freezing points are known and acceptable, and it has structural features that presumably could enhance its extinguishment capabilities. Other PAAs were rejected as candidates either because of insufficient data to make a decision or, as in the case of HCFC-31, because the chemical had known unacceptable toxic characteristics.

Table 2 groups the CAAs into those recommended for laboratory-scale testing, those that are not commercially available, and those that are considered unacceptable. Although brominated compounds exhibit superior fire suppression and explosion prevention effectiveness, regulations fostered by the Montreal Protocol prohibit future production of these chemicals. Therefore, it is recommended that such chemicals not be investigated further.

Several fluoroiodocarbons were identified that exhibit superior flame suppression capabilities although the higher molecular weight compounds do not appear to perform as well as expected for explosion prevention. The toxicity of the perfluoroiodocarbons may be sufficiently low to allow the use of these chemicals as total-flood agents. For those chemicals with boiling points above 20-30°C, an alternate means of dispersal would most likely be required. The presence of the iodine atom in the molecule is presumed to subject the compound to rapid photolytic breakdown in the lower atmosphere so that the compound would not pose a threat from a global warming or ozone depletion standpoint.

A number of halogenated ethers have been investigated as possible halon replacement agents. These include both brominated and nonbrominated compounds. Nonbrominated fluoroethers perform as physical action agents similar to hydrofluorocarbons, but uncertainty still remains as to whether the addition of the oxygen atom will reduce the atmospheric lifetime enough to limit the ODP to acceptable levels. Finally, little toxicological information exists on the haloether candidates. Consequently, a high priority is not assigned to the haloethers.

Table 2. Candidate Group List of Chemical Action Agents

Group	Name	Formula	Comment
1	Trifluoroiodomethane	CF <sub>3</sub> I	toxic?
Recommended	Pentafluoroiodoethane	CF <sub>3</sub> CF <sub>2</sub> I	toxic?
for	Perfluoro-n-propyl iodide	CF <sub>3</sub> CF <sub>2</sub> CF <sub>2</sub> I	toxic?
Lab-testing	Perfluoro-n-butyl iodide	CF <sub>3</sub> CF <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> I	toxic?
	Perfluoro-n-hexyl iodide	CF <sub>3</sub> (CF <sub>2</sub> ) <sub>4</sub> CF <sub>2</sub> I	toxic?
	4-Bromo-3,3,4,4-tetrafluoro-1-butene	CH <sub>2</sub> =CHCF <sub>2</sub> CBrF <sub>2</sub>	toxic?
2	Perfluoro-n-octyl iodide	CF <sub>3</sub> (CF <sub>2</sub> ) <sub>6</sub> CF <sub>2</sub> I	high BP*
Recommended	1,1,2,2-Tetrafluoro-dimethyl ether	CHF <sub>2</sub> OCHF <sub>2</sub>	need data
for	1,1,2,2-Tetrafluoroethyl difluoromethyl ether	CHF <sub>2</sub> OCF <sub>2</sub> CHF <sub>2</sub>	need data
Lab-testing	1,1,1-Trifluoroethyl difluoromethyl ether	CF <sub>3</sub> CH <sub>2</sub> OCHF <sub>2</sub>	need data
3	Difluoroiodomethane	CHF <sub>2</sub> I	no data
Unavailable	Fluoroiodomethane	CH <sub>2</sub> FI	carcinogenic?
Commercially	Perfluorodimethyl ether	CF <sub>3</sub> OCF <sub>3</sub>	long life?
	Methyl trifluoromethyl ether	CH <sub>3</sub> OCF <sub>3</sub>	expensive, flammable
	Difluoromethyl fluoromethyl ether	CHF <sub>2</sub> OCH <sub>2</sub> F	no data
	Trifluoromethyl difluoromethyl ether	CF <sub>3</sub> OCHF <sub>2</sub>	no data
	Trifluoromethyl pentafluoroethyl ether	CF <sub>3</sub> OCF <sub>2</sub> CHF <sub>2</sub>	not available
	Perfluorooxetane	-CF <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> O-	long life
	1,1,1-trifluoroisopropyl trifluoromethyl ether	CF <sub>3</sub> (CH <sub>3</sub> )CHOFCF <sub>3</sub>	not available
	Perfluorodimethoxymethane	CF <sub>3</sub> OCF <sub>2</sub> OCF <sub>3</sub>	no data
	Difluoromethyl bromodifluoromethyl ether	CHF <sub>2</sub> OCBrF <sub>2</sub>	no data
	Trifluoromethyl bromodifluoromethyl ether	CF <sub>3</sub> OCBrF <sub>2</sub>	no data
	Difluoromethyl bromotetrafluoroethyl ether	CHF <sub>2</sub> OCF <sub>2</sub> CBrF <sub>2</sub>	need data
	Methyl bromodifluoromethyl ether	CH <sub>3</sub> OCBrF <sub>2</sub>	no data
	3-Bromo-3,3-difluoropropene	CH <sub>2</sub> =CHCBrF <sub>2</sub>	mutagenic
	3-(Bromodifluoromethyl)-3,4,4,4-tetrafluoro-1-butene	CH <sub>2</sub> =CHC(CBrF <sub>2</sub> )FCF <sub>3</sub>	not available
	1-Bromo-3,3,3-trifluoro-1-propene	BrCH=CHCF <sub>3</sub>	mutagenic?
	2,3-Dibromo-3,3-difluoro-1-propene	CH <sub>2</sub> =CBrCBrF <sub>2</sub>	mutagenic
	4-Bromo-3-chloro-3,4,4-trifluoro-1-butene	CH <sub>2</sub> =CHCClFCBrF <sub>2</sub>	mutagenic
	3-Bromo-1,1,3,3-tetrafluoro-1-propene	CF <sub>2</sub> =CHCBrF <sub>2</sub>	highly toxic?
	1,2-Dibromo-3,3,3-trifluoro-1-propene	BrCH=CBrCF <sub>3</sub>	mutagenic?
4	Perfluoroisopropyl iodide	CF <sub>3</sub> CFICF <sub>3</sub>	too toxic
Unacceptable	1,1-Difluoroethyl fluoromethyl ether	CHF <sub>2</sub> CH <sub>2</sub> OCH <sub>2</sub> F	flammable? available?
	Dibromofluoromethane	CHBr <sub>2</sub> F	high ODP**
	1,2-Dibromo-1,1,2-trifluoroethane	CBrF <sub>2</sub> CHBrF	highly toxic, ODP
	2,2-Dibromo-1,1,1-trifluoroethane	CHBr <sub>2</sub> CF <sub>3</sub>	highly toxic, ODP
	2,3-Dibromo-1,1,1-trifluoropropane	CF <sub>3</sub> CHBrCH <sub>2</sub> Br	highly toxic, ODP
	Bromodifluoromethane	CHBrF <sub>2</sub>	high ODP
	2-Bromo-1,1,1,2-tetrafluoroethane	CF <sub>3</sub> CHBrF	high ODP

\* BP = Boiling point.

\*\* ODP = Ozone depletion potential.

A survey of the toxicological aspects of bromofluoroalkenes reveals that few of these chemicals have sufficiently low toxicities to allow their use as halon replacement agents. Many of the 2- and 3-carbon

candidates are most likely carcinogenic. Only haloalkenes with 4 or more carbons will possibly be nonmutagenic and non-carcinogenic. The molecular weights of the 4 or more carbon haloalkenes are

ranked relatively high compared to Halon 1301, which will reduce the apparent effectiveness if expressed on a weight equivalency basis.

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*The complete report, entitled "Low Ozone-Depleting Halocarbons As Total-Flood Agents: Volume 1—Candidate Survey," (Order No. PB96-109061; Cost: \$27.00, subject to change) will be available only from*

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