SURVEY OF CANDIDATE FIRE EXTINGUISHING AGENTS

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INTRODUCTION

The halogenated aliphatic hydrocarbons offer the most promise for halon alternative firefighting agents because of their cleanliness, effectiveness, and three-dimensional extinguishment characteristics. We are evaluating chemicals using a parallel-path approach, which simultaneously considers fire extinguishment, environmental characteristics, materials compatibility, availability, toxicity, agent stability, and other properties to prioritize candidates for consideration. This is the most cost-effective, timely, and promising approach. The purpose of this paper is to examine alternative fluorine-containing halogenated aliphatic hydrocarbons that have low ozone depletion and global warming potentials (ODPs and GWPs). Fluorine-containing chemicals are being emphasized to decrease the possibility of hepatotoxicity.

Fluorine-containing halocarbons can be divided into three groups, depending on the amount of toxicity data available. Group 1 chemicals are defined as those that have been produced in bulk in the recent past, are now being produced, or are being developed for near-term bulk production, and for which significant toxicity studies, up to and including chronic studies, have been performed or are now in progress. For the most part, Group 1 materials are the hydrochlorofluorocarbons (HCFCs), perfluorocarbons (FCs), and hydrofluorocarbons (HFCs) that are now being considered as substitutes for the fully halogenated chlorofluorocarbons (CFCs) in such applications as refrigeration and foam blowing. Group 1 chemicals are proposed for the short-term objective of producing alternative agents to replace Halon 1211 in firefighter training. This paper focuses on these Group 1 chemicals.

Group 2 chemicals are materials that are expected to have low toxicities, but for which limited toxicity information is available. HCFCs, FCs, and HFCs other than those in Group 1 fall in this group. Selected members of this family in combination with Group 1 chemicals are candidates for first-generation agent alternatives for Halon 1211 streaming applications. The use of blends to promote synergism or to enhance deliverability will help alternative agents approach the effectiveness of Halon 1211.

Presented at the International CFC & Halon Conference, October 10-11, 1989, Washington, DC.

Group 3 chemicals are materials that are expected to have very good, even superior, fire extinguishment capabilities, but which are suspect for toxicity and have little or no toxicity data available. The hydrobromofluorocarbons (HBFCs) and highly chlorinated halocarbons fall into this category. Unsaturated compounds are also included in this group. These chemicals could provide second-generation superior alternative agents.

For comparison, the properties of the current streaming agents Halons 1211 and 2402, plus the properties of a desired training agent, are listed in Table 1.

TABLE 1. PROPERTIES OF CURRENT STREAMING AGENTS AND DESIRED TRAINING AGENTS.

	Halon 1211	Halon 2402	Training agent (desired properties)
Flame suppression concentration, % (cup burner test)	3.2	4.2	< 10
ODP relative to CFC-11 = 1.0	2.7	11.7	< 0.05
Boiling point, °C	-3	47	-15 to 60
Vapor pressure at 25 °C, psia	33	< 10	5-40
Gas heat capacity, cal/g- °C at 25 °C	0.11	0.11	> 0.09
Heat of vaporization, cal/g	32	27.6	> 25
Toxicity, TLV[a], %	5	0.1	> 3
Cost per lb, $	2-4	2-4	< 10

[a]TLV = Threshold Limit Value for 1-minute exposure in humans.

Table 2 lists selected Group 1 candidates. Compounds were not excluded because they are poor flame suppression agents. A poor flame suppression agent could be mixed with a more effective agent to provide desirable physical properties and improved deliverability.

TABLE 2. GROUP 1 MATERIALS.

Halocarbon no.	Formula	Name
14	CF_4	Perfluoromethane (tetrafluoromethane)
21	$CHCl_2F$	Dichlorofluoromethane
22	$CHClF_2$	Chlorodifluoromethane
123	$CHCl_2CF_3$	2,2-Dichloro-1,1,1-trifluoroethane
124	$CHClFCF_3$	2-Chloro-1,1,1,2-tetrafluoroethane
132b	$CClF_2CH_2Cl$	1,2-Dichloro-1,1-difluoroethane
134a	CF_3CH_2F	1,1,1,2-Tetrafluoroethane
141b	CCl_2FCH_3	1,1-Dichloro-1-fluoroethane
142b	$CClF_2CH_3$	1-Chloro-1,1-difluoroethane
143a	CF_3CH_3	1,1,1-Trifluoroethane
152a	CHF_2CH_3	1,1-Difluoroethane
C318	cyclo-C_4F_8	Perfluorocyclobutane (octafluorocyclobutane)

TOXICITY TESTING

Toxicity testing is the most time-consuming task associated with developing firefighting agents. With accelerated testing, thorough testing of a new compound requires up to six years. Considerations of the short- and long-term health hazards to exposure, the relationships between chemical structure and toxic effects, and the biodegradation and production of reactive metabolites are of key importance when deciding which compounds hold potential for future use as firefighting agents.

Human and animal research indicates several principal health effects of halogenated hydrocarbons. First, they can stimulate or suppress the central nervous system (CNS) to produce symptoms ranging from lethargy and unconsciousness to convulsions and tremors. Second, halogenated hydrocarbons can cause cardiac arrhythmias and can sensitize the heart to epinephrine (adrenaline). Serious arrhythmias are of particular concern because firefighters are exposed to these compounds while under highly stressful conditions, when their bodies have high levels of circulating epinephrine. Third, inhalation of halogenated hydrocarbons can produce bronchoconstriction, reduce pulmonary compliance, depress respiratory volume, reduce mean arterial blood pressure, and produce tachycardia (rapid heartbeat). Fourth, these agents can cause organ damage due to degradative by-products formed during metabolism. CNS effects, cardiac sensitization, and pulmonary disorders appear to be reversible upon termination of exposure to these chemicals. Organ toxicity, on the other hand, is a latent effect and sequelae (delayed effects due to the compound or its metabolites) are usual.

The relationship between chemical structure and toxicity has been explored in simple halogenated alkanes. Evidence indicates that the greater the number of fluorine atoms and the fewer the number of chlorine, bromine, and iodine atoms present on the molecule, the lower the toxicity of the compound. Even with the replacement of only one chlorine by fluorine (e.g., HCFC-22 versus 21), a notable reduction in toxicity (as indicated by exposure limits) is observed. The same trend is seen in perhalogenated methanes, where, for example, FC-14 (CF_4) is much less toxic than CFC-10 (CCl_4). Similarly, toxicity is decreased when bromine or iodine atoms are replaced by fluorine. Also, when hydrogen is replaced with fluorine, a reduction in toxicity of halocarbons occurs. The same trends hold for halogenated ethanes, propanes, and butanes, in which the reduction of toxicity is a function of increasing fluorination at the expense of chlorine. In haloalkanes of two or more carbons, when four fluorine atoms are present on the molecule, the number of hydrogen atoms appears to have little or no effect on the toxicity.

Several halocarbons exist with completed toxicological testing to support their use as alternative firefighting agents. Toxicity testing has been completed on FC-C318, HCFC-22, HCFC-142b, and HFC-152a, and will be completed at the end of 1990 for HCFC-123. For HCFC-141b, completion of toxicity testing will require 2-4 years; however, commercial production is expected earlier. For HCFC-124, toxicity testing is expected to be completed in 1994 or 1995 though commercial availability is expected two years earlier (1992-1993). Commercial production of HCFC-123 and HFC-134a will begin in 1990. Note that additional toxicity testing may be required for materials employed as fire extinguishing agents. The properties of the most promising Group 1 candidates are summarized in Table 3.

WORK IN PROGRESS

More than 50 Group 1, 2, and 3 candidates have been tested at laboratory-scale and some at medium-scale. Small-scale testing of selected blends will soon be initiated. The following compounds will be tested for use as training agents, either in blends or as neat materials: 22, 123, 124, 134a, 141b, 142b, 143a, 152a, and C318. Though they meet all the criteria above for testing in pure form, HCFCs 141b and 142b are flammable at some concentrations, and this precludes their use as pure substances.

SUMMARY

A matrix of desirable mixtures scheduled for small- and medium-scale testing is given in Table 4. The reasoning used to develop this table is that the boiling point of the mixture should be within the range of -10 °C to 50 °C to provide enough liquid character for deliverability and sufficient volatility for rapid flame knockdown. Incomplete lists of Group 2 and Group 3 candidates appear in Tables 5 and 6.

TABLE 3. PROPERTIES SUMMARY FOR CANDIDATE TRAINING AGENTS.

Halo-carbon no.	Estd. date for completion of toxicity tests	Est. flame supp. conc. (%)	Boiling point (°C)	Vapor pressure at 25 °C (psia)	Gas heat capacity (cal/g)	Heat of vaporization (cal/g)	[a]ODP	[b]GWP	Est. relative cost
[c]12B1	Completed	3.7	-3	33	0.108	[d]34	2.7	--	3
22	Completed	11.0	-41	152	0.158	[d]56	0.05	0.34	1.3
123	End of 1990	6.7	28	13	0.163	40.1	0.02	0.017	3
124	1994 - 1995	8.8	-12	–	0.197	–	0.018	–	3+
134a	Mid-1992	15.9	-27	83	0.204	50	0.00	0.025	5
141b	1992-1994	7.8	32	[e]12	0.181	53.3	0.07	0.087	3
142b	Completed	11.0	-10	[e]53	0.197	[d]57	0.05	0.34	2
143a	1992-1993	20.0	-48	[e]194	0.222	[d]56	0.00	0.72	3+
152a	Completed	28.0	-25	[e]85	0.245	[d]78	0.00	0.026	2.3
C318	Completed	11.6	-4	25	–	[d]28	[f]0.00	--	7

[a]Values calculated by Lawrence Livermore National Laboratories 1-D model, relative to CFC 11 = 1.0.
[b]Values calculated by Dupont 1-D model, relative to CFC 11 = 1.0.
[c]Halon 1211.
[d]Estimated by Trouton's Rule.
[e]Estimated from boiling point and heat of vaporization using the Clausius-Clapeyron equation.
[f]Estimated by NMERI.

TABLE 4. MATRIX OF DESIRABLE BLENDS SCHEDULED FOR TESTING.[a]

	123	124	134a	141b	142b	143a	152a	C318
22	X			X				
123		X	X	X	X	X	X	X
		124		X	X			
			134a	X				
				141b		X		X
					142b			
						143a		
							152a	

[a]X = Indicates a desirable mixture for testing as a halon alternative streaming agent for firefighter training.

TABLE 5. SELECTED GROUP 2 CANDIDATE HALON ALTERNATIVES.

Halocarbon no.	Halon no.	Name
123a	232	1,2-Dichloro-1,1,2-trifluoroethane
123b	232	1,1-Dichloro-1,2,2-trifluoroethane
124a	241	1-Chloro-1,1,2,2-tetrafluoroethane
132	222	1,2-Dichloro-1,2-difluoroethane
132a	222	1,1-Dichloro-2,2-difluoroethane
132c	222	1,1-Dichloro-1,2-difluoroethane
133	231	1-Chloro-1,1,2-trifluoroethane
133a	231	2-Chloro-1,1,1-trifluoroethane
133b	231	1-Chloro-1,1,2-trifluoroethane
134	24	Tetrafluoroethane *
141a	212	1,2-Dichloro-1-fluoroethane
143	23	1,1,2-Trifluoroethane
225	352	Dichloropentafluoropropane *
226	361	Chlorohexafluoropropane *
234	342	Dichlorotetrafluoropropane *
235	351	Chloropentafluoropropane *
236	36	Hexafluoropropane *
C325	461	Chlorohexafluorocyclobutane *
336	462	Dichlorohexafluorobutane *
337	471	Chloroheptafluorobutane *
Perfluoroalkanes:		Perfluoropropane
		Perfluorobutane
		Perfluoropentane
		Perfluorocyclopentane
		Perfluorohexane
		Perfluorocyclohexane
		Perfluorocycloheptane
		Perfluoromethylcyclohexane
		Perfluoro-1,3-dimethylcyclohexane

* Several isomers are possible.

TABLE 6. SELECTED GROUP 3 CANDIDATE HALON ALTERNATIVES.

Halocarbon no.	Halon no.	Name
22B1	1201	Bromodifluoromethane
123aB1	2311	1-Bromo-2-chloro-1,1,2-trifluoroethane
123B2	2302	Dibromotrifluoroethane *
124B1	2401	Bromotetrafluoroethane *
133B1	2301	Bromotrifluoroethane *
142B1	2201	Bromodifluoroethane *
142B1	2201	Bromodifluoroethane *
225B1	3511	Bromochloropentafluoropropane *
225B2	3502	Dibromopentafluoropropane *
226B1	3601	Bromohexafluoropropane *
234B1	3411	Bromochlorotetrafluoropropane *
235B1	3501	Bromopentafluoropropane *
243B2	3302	Dibromotrifluoropropane *
244B1	3401	Bromotetrafluoropropane *
252B1	3211	Bromochlorodifluoropropane *
253B1	3301	Bromotrifluoropropane *
262B1	3201	Bromodifluoropropane *
328B1	4801	Bromooctafluorobutane *
336B1	4611	Bromochlorohexafluorobutane *
336B2	4602	Dibromohexafluorobutane *
337B1	4701	Bromoheptafluorobutane *

* Several isomers are possible.

ACKNOWLEDGMENTS

Portions of the work described here were sponsored by the Air Force Engineering and Services Laboratory, Air Force Engineering and Services Center, Tyndall AFB, Florida 32403, under contract F08635-85-C-0129.

The authors would like to thank Major E. Thomas Morehouse, Jr., Captain John R. Floden, and Mr. Joseph L. Walker for valuable discussions and suggestions on this work.