SECOND GENERATION HALON REPLACEMENTS

Stephanie R. Skaggs
Center for Global Environmental Technologies
New Mexico Engineering Research Institute
The University of New Mexico
Albuquerque. New Mexico. USA 57131

INTRODUCTION

Halon production will cease at the end of 1993, and, as vet, the search for halon replacements has not been entirely successful. A large number of candidate replacement agents have been announced by industry for commercialization (Table I), and even more chemicals are under consideration. Yet, all of these so-called "first-generation" agents, which will be available in bulk now or in the near hture, have serious tradeotfs in one way or another. This paper deals specifically with agents that are chemically similar to the present halons and refers to these chemicals as halon "replacements"; whereas, "alternatives" are those agents that are "not-in-kind" substitutes because their chemical nature is different from halons. Alternatives include carbon dioxide, foam, water, dry chemicals, and inert gases.

Successful halon replacement agents have a minimum of four requirements: a low global environmental impact (*i. e.*, low ODP, GWP, and atmospheric lifetimes), acceptabie toxicity to suit the application, low residue (*i. e.*, clean and volatile), and effectiveness against fires andior explosions. Though it is easy to find replacements that fulfill any three of these requirements. no replacement has been found to date that meets all four. Most difficult appears to be finding replacements that have acceptable global environmental impact and an effectiveness equal to the present halons. Any replacement must, of course, also be manufacturable at an affordable cost.

Several factors influence how well candidates meet the requirements for a successful halon replacement. The first is that bromine or iodine is necessary to make a tire suppression agent diose efficiency is equal to that ofthe halons. It is well known that chemicals containing bromine or iodine suppress fires primarily by removal of combustion free radicals, a process which catalytically inhibits the combustion chain reactions (1). The second is that it is also well known that bromine in the stratosphere catalyticaily depletes ozone (2). This is also said to be true about iodine in the stratosphere. However. iodine-containing chemicals are susceptible to tropospheric

degradation by photolysis, so iodides, released from ground level, tend not to reach the stratosphere to deplete ozone. Third, bromine and iodine generally increase the toxicity of a chemical (3). Finally, chemicals containing heavy halogens such as bromine and iodine have higher boiling points than fluorocarbons. Increasing the boiling point tends to decrease the volatility, and, hence, the cleanliness. Thus, the factor that promotes a high effectiveness (presence of bromine or iodine) also produces detrimental effects in terms of the environmental impact, health effects, and cleanliness.

TABLE 1. FIRST GENERATION HALON REPLACEMENT CANDIDATES

Candidate	Chemical Formula	Commercialization as Halon Replacement
HBFC-22B1	CHF_2Br	Great Lakes (FM 100)
HCFC-22	$CHClF_2$	
HCFC-123	CF_3CHCl_2	Du Pont (FE 232)
HCFC-124	CF_3CHClF	Du Pont (FE 241)
	Hydrofluorocarbons	
HFC-23	CHF_3	Du Pont (FE 13)
HFC-32	CH_2F_2	
HFC-125	CF_3CHF_2	Du Pont (FE 25)
HFC-134a	CF_3CH_2F	
HFC-227ea	CF_3CHFCF_3	Great Lakes (FM 200)
	Perfluorocarbons	
FC-3-1-10	C_4F_{10}	3M Chemicals (PFC 410)
FC-5-1-14	C_6F_{14}	3M Chemicals (PFC 614)
	Proprietary	
NAF S-III	Blend (Primarily HCFCs)	NAF Fire Guardian
NAF P	Blend (Primarily CFCs)	NAF Fire Guardian
Halotron I	Blend (Primarily HCFC)	American Pacific Corp.

IDEAL HALON REPLACEMENTS

If the factors that influence the requirements of a successful halon replacement (effectiveness, short atmospheric lifetime, low toxicity, and cleanliness) are considered, the features of what could be called the "ideal halon replacement" can be theorized (Figure 1). The wavy lines in the center represent a theoretical molecule. The ideal halon replacement would contain either bromine or iodine in order to be an effective fire and explosion suppressant. This feature requires that some chemical feature also be present in order to reduce the tropospheric

lifetime, so that the chemical does not reach stratospheric ozone. Chemical features known to reduce the atmospheric lifetime include the presence of unsaturated carbon bonds, polar substituents such as oxygen, and iodine atoms (4). Unsaturated compounds (those containing carbon-carbon double bonds, C=C) are susceptible to degradation by reaction with hydroxyl free radicals in the troposphere. Atmospheric lifetimes of polar-substituted compounds may be reduced by water solubility, which allows the chemical to be "rained out" of the atmosphere. The presence of iodine atoms allows tropospheric photolysis, which reduces the atmospheric lifetime of the chemical. Thus, incorporation of any of these features into a chemical reduces the atmospheric lifetimes.

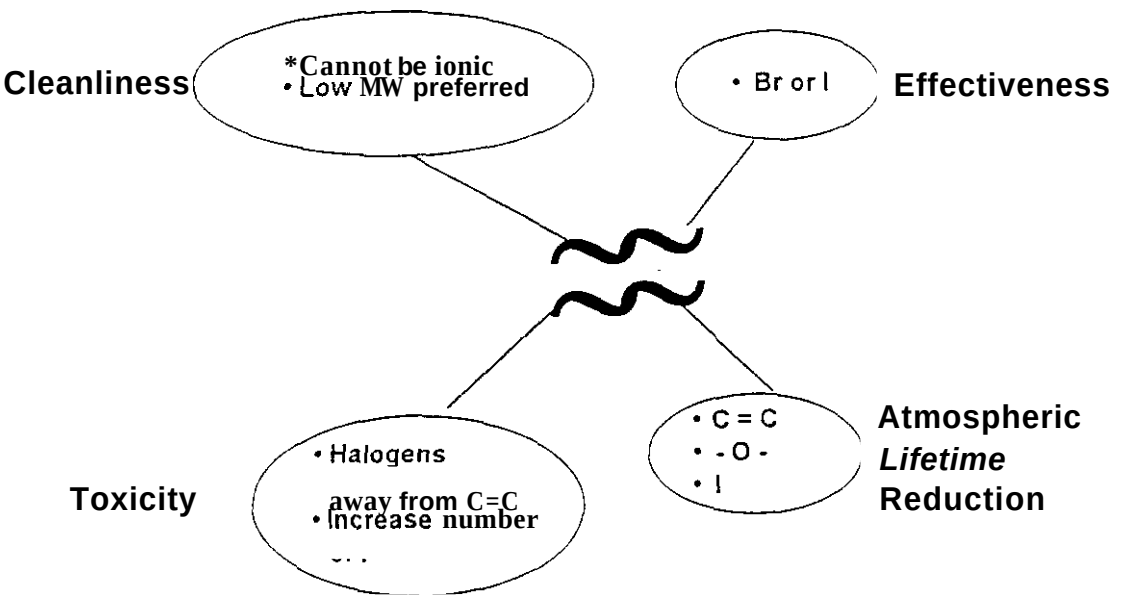

Figure 1. Ideal Halon Replacement

Given that an ideal halon replacement contains bromine or iodine for effective tire suppression and either unsaturated carbon bonds, polar-substituents, or iodine atoms for reduced atmospheric lifetimes, the molecule must also incorporate features which reduce the toxicity. Increasing the number of fluorine atoms on the molecule helps to reduce the toxicity of chemicals with any of the features that reduce atmospheric lifetimes. A comprehensive survey of toxicological literature indicates that in order for the toxicity to be lowest for chemicals containing unsaturated carbon bonds, halogens (fluorine, bromine, or chlorine) must be away from the double bond.

Finally, to achieve cleanliness. the ideal halon replacement must not be ionic and a low molecular weight is preferred in order to increase the agent volatility. The challenge, therefore, is

to identify candidates which encompass chemical features that satisfy all the requirements for a successful halon replacement.

Three general families containing chemicals with the above features have been identified: bromofluoroalkenes, polar-substituted bromocarbons such as bromofluoroethers. and fluoroiodocarbons. Bromofluoroalkenes contain unsaturated carbon-carbon double bonds. Bromofluoroethers contain oxygen atoms attached to carbons by single bonds. Obviously, fluoroiodocarbons contain iodine atoms.

The U. S. Environmental Protection Agency **(EPA)** has been the primary sponsor of a program to investigate these three classes of chemicals as Halon 1301 total flooding agents for use particularly at the Alaskan North Slope oil and gas production facilities (5). These facilities currently utilize Halon 1301 for fire suppression and explosion prevention.

The EPA program includes compiling all existing information on physical properties, availability and cost, toxicity, and global environmental characteristics of selected representatives from each of these chemical classes. Approximately 40 candidates were considered. Once all known information was collected, a number of chemicals were tested at laboratory scale fire suppression capabilities. The following discussion presents a brief overview of the findings.

BROMOFLUOROALKENES

Bromofluoroalkenes are fluorocarbons that contain a carbon-carbon double bond in addition to bromine. The presence of the bromine atom enhances the flame suppression capability. The double bond leads to a short atmospheric lifetime due to rapid reaction with hydroxyl free radicals in the troposphere. The toxicity of this type of chemical has not been fully studied; however, evidence does indicate that halogens (fluorine. bromine) must not be bound to the carbon-carbon double bond because this leads to an electron deficient site susceptible to nucleophilic attack. Nucleophilic attack results in a high toxicity. Also, bromine atoms *alpha* or *beta* to a double bond often leads to mutagenicity. Therefore, bromofluoroalkenes of 4 carbons or more may be required to prevent mutagenic effects. However, 4-carbon bromofluoroalkenes have high boiling points and may require misting for total flood applications. Bromofluoroalkenes with boiling points less than 150°C are probably sufficiently volatile to be clean. Table 2 presents information on boiling points, flame extinguishment concentration determined in the cup burner, and toxicity information on selected bromofluoroalkenes. A survey of commercial manufacturers

indicates that several bromofluoroalkenes are available in limited quantities, but are generally less easy to manufacture than bromofluoroalkanes (no carbon-carbon double bonds).

TABLE 2. SELECTED BROMOFLUOROALKENES

CHEMICAL	BOILING POINT, °C	EXTINGUISHING CONCENTRATION, vol %	TOXICITY
$CF_2BrCF_2CH=CH_2$	55	3.5	Mouse 1-hour LC_{50} > 1% (6), probably not mutagenic
$CF_2BrCF_2CH=CH_2$	SO	?	Probably not mutagenic

BROMOFLUOROETHERS

Bromofluoroethers contain an oxygen-atom bound to *2* carbons. The bromine atom enhances the fire suppression effectiveness. The oxygen helps reduce the atmospheric lifetime through rainout, thus, lowering the ODP and GWP. Some questions still remain as to whether this shortened atmospheric lifetime will be low enough to eliminate problems with ozone depletion. The toxicity of bromofluoroethers has been investigated in the past because these kinds of chemicals have been considered as clinical anesthetics. Evidence indicates that, like halocarbons, highly tluorinated ethers are the least toxic. Diethyl ethers *(e.;:.,* $CHBrFCF_2$-O-$CHFCH_3$) are the least toxic. Fully halogenated ethers tend to be convulsants and hydrogen-containing halogenated ethers tend to be anesthetic. Therefore. a balance must be achieved between the number of halogen and hydrogen atoms to give a chemical that is neither too anesthetic nor convulsant. Table 3 is a summary of boiling points, extinguishing concentrations determined in the cup burner, and the toxicity of selected bromofluoroethers. Bromotluoroethers are generally volatile and clean if the molecular weight is below 400. A survey ofthe availability of brornofluoroethers has revealed that none are being manufactured commercially

TABLE 3. SELECTED BROMOFLUOROETHERS			
CHEMICAL	BOILING POINT, °C	EXTINGUISHING CONCENTRATION, vol %	TOXICITY
CF_2Br-O-CF_2H	25	?	Probably anesthetic
$CHBrFCF_2$-O-CH_3	89	?	Potent anesthetic, does not produce cardiac sensitization (7)
CF_2Br-O-CF_3	-5.4	?	Probably convulsant

FLUOROIODOCARBONS

Fluoroiodocarbons are extremely effective fire suppressants. Flame extinguishing concentrations of fluoroiodocarbons are generally in the same range as bromocarbons, 2-3%. Iodine also helps reduce the tropospheric lifetime through photolysis, which reduces the ODP and GWP. The toxicological evaluation of fluoroiodocarbons indicates that fully fluorinated iodocarbons have the lowest toxicity. Conversely, fluoroiodocarbons containing hydrogen atoms are generally potent anesthetics. For example, CF_3CH_2I is anesthetic at concentrations of 1.25% in mice exposed for 10 minutes (8). However, fully fluorinated iodocarbons are much less anesthetic because they lack acidic hydrogens (hydrogens on carbons also bound to halogens). For example, CF_3CF_2I was found to be anesthetic in mice and rats given 10% concentration, but not in dogs or monkeys (9). In fact, not even 50% was anesthetic in monkeys. However, cardiac arrhythmias were noted within minutes of exposure. Table 4 is a summary of boiling points, extinguishing concentrations determined in the cup burner, and the toxicity of selected tluoroiodocarbons. Fluoroiodocarbons are generally clean if they contain less than 6 carbon atoms because of sufficiently low boiling points and volatility. Those chemicals with boiling points above a nominal 30°C would likely require misting to disperse in a total-flooding application. For example, $CF_3(CF_2)_4CF_2I$ has a boiling point of 117°C. Accordingly, fluoroiodocarbons containing *2* or more carbons may require misting. Several fluoroiodocarbons are available at prices ranging between $300/lb and $500/lb. The lower price reflects the approximate cost for 100 lbs or more of CF_3I.

CHEMICAL	BOILING POINT, 'C	EXTINGUISHING CONCENTRATION. vel %	TOXICITY
*CF_3I	-23	3.0	Not lethal in dogs at 50% concentration (10)
CF_3CF_2I	13	7.1	Mouse I-hour LC_{50} > 1 % (6)
$CF_3CF_2CF_2I$	41	3.0	Unknown

* Available in 100 lb quantities

CONCLUSIONS

In conclusion. a number of highly effective fire fighting chemicals have been identified that appear to have short atmospheric lifetimes and low ODPs and GWPs. A number of questions still remain unanswered concerning toxicity, corrosivity, manufacturability, and long-term stability. Unfortunately, the interest in these chemicals may not be sufficiently large to justify the cost of answering these questions.

Nonetheless, it is recommended that toxicity screens be performed on the best candidates from each chemical class. To identify other candidates, it would also be desirable to perform a comprehensive survey of other chemical classes. Trifluoroiodomethane (CF_3I) is recommended to be tested at field scale since it is commercially available in field test quantities. Other questions concerning agent stability, bulk manufacturability, and toxicity should also be addressed. Finally, it is recommended that further investigation be done on halocarbon misting technology since many of the identified second-generation chemicals have boiling points higher than Halon 1301, now used for total Hooding applications. Misting will allow a larger number of candidates to be considered for this application.

ACKNOWLEDGMENTS

This work was supported by the U. S. Environmental Protection Agency, Air and Energy Engineering Research Laboratory (AEERL), the North Slope oil and gas companies. and the U. S. Coast Guard.

REFERENCES

1. Rosser, W. A., Wise, H., and Miller, J., "Mechanism of Combustion Inhibition by Compounds Containing Halogen," *Seventh Symposium (International) on Combustion*, London and Oxford, 28 August - 3 September 1958, Butterworths Scientific Publications, London, 1959, pp. 175-182.

2. Luther, F. M., Chang, J. S., Wuebbies, D. J., and Penner, J. E., "Ozone Depletion Calculations," *Proceedings of the NATO Advanced Research Institute on the Effects of Solar Ultraviolet Radiation on Marine Ecosystems*, Copenhagen, Denmark, 28-31 July 1980.

3. Di Poalo, T. and Sandorfy, C., "Hydrogen Bond Breaking Potency of Fluorocarbon Anesthetics," *Journal of Medicinal Chemistry*, Voi. 17, No. 8, 1974, pp. 809-814.

4. Walters, E. A. and Molina, M. J., "Global Environmental Characteristics of Second Generation Halon Replacements," Halon Alternatives Technical Working Conference 1993, Albuquerque, New Mexico, 11-13 May 1993.

5. Skaggs, S. R. and Tapscott, R. E., "Candidate Survey, Laboratory Testing, and Recommendations on Far Term Halon Replacement Agents," U. S. Environmental Protection Agency, Air and Energy Engineering Research Laboratory, Contract Number CR-817774-01-0, Research Triangle Park, North Carolina, May 1993.

6. Ulm, K., "Screening Results on the Toxicity of Numerous Fluoro Organic Compounds," *Abstracts of the International Symposium on Fluorine Chemistry*, Paris. France, 1986, pp.252.

7. Atrusio, J. F., Jr. and van Poznak, A., "Laboratory and Clinical Studies with 1,1,2-Trifluoro-2-bromoethyl Methyl Ether," *Federation Proceedings*, Vol. 20, No. 1, 1961, pp. 312.

8. Robbins. B. H., "Preliminary Studies of the Anesthetic Activity of Fluorinated Hydrocarbons," *Journal of Pharmacology and Experimental Therapy*, Vol. 86, 1946. pp. 197-204.

9. Krantz, J. C., Jr. and Rudo, F. G., "The Fluorinated Anesthetics," Chapter 10, Handbook of Experimental Pharmacology, Vol XX/I, edited by F. A. Smith, Springer-Verlag, West Berlin, 1966, pp. 501-564.

10. Lu, G. G., Ling, J. S. L., and Krantz, J. C.. Jr., "Anesthesia XLI. The .Anesthetic Properties of Certain Fluorinated Hydrocarbons and Ethers," *Anesthesiology*, Vol. 14. 1953, pp. 466-472.