REPLACEMENT AGENTS - AN HISTORICAL OVERVIEW

Robert E. Tapscott
Center for Global Environmental Technologies
NMERI, University of New Mexico

This is a very **brief** overview of the history of the development of halon replacement agents (Overhead **1).**

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Overhead 1

When discussing halon substitutes, we must be careful to distinguish between alternatives (non-halon-like) agents and replacement agents (halocarbons) (Overhead **2). This** overview treats only replacement agents.

SUBSTITUTE AGENTS FOR HALONS

- Alternatives (Non-Halon-Like)
- Replacements **(Halocarbons)**

Overhead **2**

The present candidate replacement agents must be termed "first-generation replacements" (Overhead **3). All** of the first-generation replacement agents **are** either lower efficiency (compared to present halons), low-ODP extinguishants or they **are** high-efficiency, higher ODP agents. None of these candidate agents has both a low ODP and an efficiency equal to that of the present halons across all applications. In specific applications (e.g., explosion suppression, small Class B fires), however, some first-generation halon replacement agents may be as effective **as** the present halons.

SUBSTITUTE AGENTS DEVELOPMENT

- First-Generation
  - Lower Efficiency, Low-ODP Agents or
  - High Efficiency, Higher ODP Agents

- Second-Generation
  - High Efficiency, Low-ODP Agents

Overhead 3

Halon replacements can be divided into two types: physical action agents (PAAs) and chemical action agents **(CAAs)** (Overhead **4).**

EXTINGUISHMENT MECHANISMS

- Physical (Physical Action Agents: PAAs)
- Chemical (Chemical Action Agents: CAAs)

Overhead **4**

Physical extinguishment can occur by a variety of mechanisms (Overhead 5); however, vapor-phase cooling appears to be the most important for the PAA halon replacements.

PHYSICAL EXTINGUISHMENT MECHANISMS

- Vapor-Phase Heat Absorption
- Liquid-Phase Heat Absorption
- Evaporative Cooling
- Thermal Dissociation
- Dilution of Fuel and Oxygen
- Separation of Fuel and Oxygen

Overhead 5

Chemical extinguishment occurs primarily by removal of combustion free radicals (Overhead 6).

CHEMICAL EXTINGUISHMENT MECHANISMS

- Removal of Hydrogen Free Radicals
- Removal of Hydroxyl Free Radicals
- Free Radical Recombination

Overhead 6

In general, development of halon replacement agents has proceeded from consideration of HBFCs (hydrobromofluorocarbons) through consideration of HFCs (hydrofluorocarbons) (Overhead 7). Note, however, that some families were considered simultaneously. The environmental characteristics improve (ODPs and GWPs decrease) as we go down the list from HBFCs to HFCs; however, the efficiency (with some exceptions) tends to decrease in the same direction.

CLASSES OF FIRST-GENERATION AGENTS

- HBFCs (Hydrobromofluorocarbons)
- CFCs (Chlorofluorocarbons)
- HCFCs (Hydrochlorofluorocarbons)
- FCs (Perfluorocarbons)
- HFCs (Hydrofluorocarbons)

Overhead 7

Since we will be looking at some selected information for halon replacements, we need to first **look** at corresponding information for the halons now used in the **U.S.** -primarily, Halon 1301 and 1211 (Overhead **8).** The boiling point of an agent is probably the single most important factor in determining whether that chemical is most suitable for total-flood or for streaming. Materials with low boiling points are best used for total flood, while those with high boiling points will be targeted toward streaming. Though there is no clear division point, chemicals with boiling points lower than approximately -20 °C are probably too gaseous to be used effectively in most streaming applications.

HALONS				
Halons	BP, °C	Ext. Conc., %	ODP	LC_{50}/ALC, %
1301	-58	2.9	~16	>80
1211	-4	3.2	~4	>13

Overhead 8

The extinguishment concentrations given in this overhead are the concentration in the gas phase needed to extinguish an n-heptane fire as determined in a cup burner. Though this number gives some measure of the effectiveness of an agent (in general, a lower extinguishment concentration indicates a higher effectiveness), it can be very misleading. First, for streaming agents, the physical properties (particularly, the boiling point and vapor pressure) are at least as important as the inherent fire extinguishment ability. For example, Halon 1301, a very gaseous agent, is an ineffective streaming agent for large, outdoor fires despite its very low extinguishment concentration. Cup burner data are best used for predicting the effectiveness in total-flood applications. Second, in many cases, what is important is not the gas-phase concentration needed but the weight or the storage volume required. Nevertheless, the gas-phase extinguishment concentration is often presented, and we are doing so here.

Many, but not all, of the ozone depletion potentials (ODPs) given in this presentation are the values presented in the 1991 UNEP assessment of the Montreal Protocol (Reference 1). In many cases, these values differ from those cited in the original Protocol (Reference 2).

The LC_{50} values give some indication of the acute toxicity of a compound. For the most part, the values given here are *in-vivo* values obtained in four-hour rat studies. Note that other toxicity data, such as cardiac sensitization, may be more important in assessing allowable exposure levels for use.

Work on halon replacements resulting from ozone depletion concerns did not really begin until the fall of 1976, when the possible impact of halons on stratospheric ozone first became apparent to the user community. This is not to say, however, that the need for halon replacements had not been considered earlier by some individual researchers.

Among the first agents to be given serious attention were the hydrobromofluorocarbons (HBFCs) (Overhead 9). These chemical action agents (CAAs) can be considered to be obtained from a halon by substitution with hydrogen. The presence of a hydrogen atom makes the chemical reactive with tropospheric hydroxyl free radicals, which serve to remove many pollutants from our atmosphere. The first report of the possible use of HBFCs as chemical replacements for halons was made in the fall of 1989 when HBFC-22B1 (and some other hydrobromofluorocarbons) was discussed at the International Conference on CFC arid Halon Alternatives (Reference 3). It should be noted, however, that this agent was actually first assessed in a study by Purdue University from 1947 to 1950 (Reference 4). The HBFCs are exceedingly effective agents; however, they have relatively high ODPs, making their potential for use questionable.

HBFCs

- CAAs
- Very Effective
- Relatively High ODPs

Overhead 9

Two HBFC agents have been announced as candidate halon replacements—**HBFC-22B1**, bromodifluoromethane (**CHF_2Br**), and HBFC-124B1, **2-bromo-1,1,1,2-tetrafluoroethane** (CF_3CHBrF) (Overhead 10). HBFC-124B1 would probably be best used as a streaming agent. The physical propemes of HBFC-22B1 indicate that it could be used for either streaming or total flood. Both agents are highly effective; however, they have relatively high ODPs.

HBFC CANDIDATES

HBFC	BP, C	Ext. Conc., %	ODP	LC_{50}, %
22B1	-15	3.9	~1.4	11
124B1	8	3.6	0.3-0.4	

Overhead 10

In some of the very early work, before the seriousness of ozone depletion had been completely realized, CFCs (chlorofluorocarbons) received some attention as halon replacements (Reference 5). Some of the test results, particularly on blends, showed a very high effectiveness. In general, these agents appear to be among the most effective of the PAAs; however, these materials have relatively high ODPs and are subject to severe regulatory restrictions (Overhead 11). At least one proprietary blend of CFCs is being marketed.

CFCs

- PAAS
- Relatively Effective
- Relatively High ODPs
- Proprietary Blends

Overhead 11

In order to reduce the ODPs from those of the HBFCs and the CFCs, researchers turned to HCFCs, hydrochlorofluorocarbons(Overhead 12). The ODPs of these chemicals are low (but not zero) because they contain no bromine and because they contain hydrogen, which reduces the atmospheric lifetime. Unfortunately, they have lower efficiencies than those of the halons and HBFCs.

HCFCs

- PAAS
- Low ODPs
- Less Effective Than Halons

Overhead 12

Three HCFCs have received a great deal of attention as halon replacements —HCFC-22, chlorodifluoromethane ($CHClF_2$); HCFC-123, 2,2-dichloro-1,1,1-trifluoroethane (CF_3CHCl_2); and HCFC- 124.2-chloro-1,1,1,2-trifluoroethane (CF_3CHClF) (Overhead 13). The ODPs of these materials are very low, as are the acute toxicities, except possibly for HCFC-123. HCFC-123 would appear to have the greatest potential as a streaming agent. The other two chemicals would probably be used primarily in total-flood applications.

HCFC CANDIDATES				
HCFC	BP, °C	Ext. Conc., %	ODP	LC_{50}, %
22	-41	11.6	0.055	27-30
123	24	6.3	0.02	3.2
124	-12	8.2	0.022	23-36

Overhead 13

As the regulatory restrictions and environmental effects of ozone-depleting substances have become better defined, researchers have looked more and more at compounds that contain no chlorine or bromine — the perfluorocarbons (FCs) and the hydrofluorocarbons (HFCs). Both of these families of chemicals have zero ODPs. The FCs have extremely low toxicities, probably the lowest of any of the families of halocarbons being considered as halon replacements (Overhead 14). Like the other PAAs, the efficiencies of FCs are lower than those of the halons across a broad range of applications. However, for specific applications, the effectiveness of a specific compound may be as good as the present halons or at least acceptable. There is, however, a concern about the long atmospheric lifetime (and, therefore, the GWPs) of the perfluorocarbons.

FCs

- PAAS
- Zero ODPs
- Very Low Toxicities
- Longer Atmospheric Lifetimes
- Less Effective Than Halons

Overhead 14

Three perfluorocarbons have been seriously considered as halon replacements (Overhead 15). There is some concern about possible perfluoroisobutene (PFIB) formation in flames by C-318 (perfluorocyclobutane). FC-3-1-10 (perfluorobutane) is a candidate for total-flood and FC-5-1-14 (perfluorohexane) is a candidate for streaming.

FC CANDIDATES				
FC	BP, °C	Ext. Conc., %	ODP	LC_{50}, %
C-318	-6	7	0.0	V.Low Tox.
3-1-10	-5	5.5	0.0	V.Low Tox.
5-1-14	56	4.4	0.0	V.Low Tox.

Overhead 15

To reduce the atmospheric lifetime, while keeping the ODP at zero, HFCs are being examined as halon replacements (Overhead 16). As a group, these materials have the lowest environmental impacts of any of the candidate replacement agents. However, like the other PAAs, their effectiveness is lower than that of the halons and they, like the others, appear to have relatively high decomposition product emissions when exposed to fires.

HFCs

- **PAAS**
- Zero ODPs
- Relatively Low Toxicities
- Shorter Atmospheric Lifetimes
- Less Effective Than **Halons**
- Indication of High Decomposition Product Emissions

Overhead 16

A number of HFC candidates are being seriously considered as halon replacements (Overhead 17), and some of these are being commercialized. Most of these are primarily total-flood candidates; however, the properties of HFC-227ea are such that it could also be considered as a streaming candidate.

HFC CANDIDATES				
HFC	BP, °C	Ext. Conc., %	ODP	LC_{50}
23	-82	12.4	0.0	66
32	-52	9.0	0.0	>76
125	-49	9.4	0.0	70
134a	-27	10.5	0.0	50
227ea	-16.4	5.9	0.0	80

Overhead 17

A summary of all of the fist-generation candidates is shown in Overhead 18. This list also includes, as a general category, proprietary agents, which are primarily blends or formulations.

FORMULAS	
HBFC-22B1	CHF_2Br
HBFC-124B1	CF_3CHBrF
HCFC-22	$CHClF_2$
HCFC-123	CF_3CHCl_2
HCFC-124	CF_3CHClF
C-318	$-(CF_2)_4-$
FC-3-1-10	C_4F_{10}
FC-5-1-14	C_6F_{14}
HFC-23	CHF_3
HFC-32	CH_2F_2
HFC-125	CF_3CHF_2
HFC-134a	$CF3CH_2F$
HFC-227ea	CF_3CHFCF_3
Proprietary	Blends or Formulations

Overhead 18

Since all of the first-generation agents either have higher ODPs or are less effective than the existing halons over the broad spectrum of applications, a search is now underway for second-generation agents that have both low ODPs and high efficiencies (Overhead 19). This can be done by looking at additional mechanisms to reduce tropospheric lifetimes while keeping the substituents — iodine or bromine — that allow chemical action (Reference 6).

Among the mechanisms that allow decreased tropospheric lifetime are reaction of a carbon-carbon double bond with hydroxyl free radicals (alkenes), photolysis (alkenes, iodides, and geminal dibromides), and rainout (polar molecules). Some of these classes of chemicals are now being tested; however, even if found acceptable, fielding will require several years due to the requirements for toxicity testing and manufacturing capabilities.

SECOND GENERATION AGENTS

- Bromoalkenes
  - Reaction with Hydroxyl Free Radicals
  - Photolysis
- Iodides
  - Photolysis
- Hydrogen-Containing Geminal Dibromides
  - Reaction with Hydroxyl Free Radicals
  - Photolysis
- Polar-Substituent Bromocarbons
  - Rainout

Overhead 19

REFERENCES

1. *UNEP Scientific Assessment Panel Report,* p. 6-16, 1991.

2. United Nations Environment Programme, ***Montreal Protocol** on **Substances that Deplete the Ozone Layer—Final Act,*** 1987.

3. Moore, J. **P.,** Moore, T. A., Salgado, D. **P.,** and Tapscott, R. E., "Halon Alternatives Extinguishment Testing," International Conference on CFC and Halon Alternatives, Washington, DC, 10-11 October 1989.

4. ***Fire Extinguishing Agents*,** Purdue Research Foundation and Department of Chemistry, Purdue University, W. Lafayette, IN, with Army Engineers Research and Development Laboratories, Fort Belvoir, VA, Final Report for Contract **W44009-ENGR-507, 1950,** AD654322.

5. Tapscott, R. E., Lee, M. E., Watson, J. D., Nimitz, J. S., and Rodriguez, M. L., ***Next-Generation Fire Extinguishing Agent. Phase IV—Foundation for New Training Agent Development,*** ESL-TR-87-03, Vol. 4 of 5, Air Force Engineering and Services Laboratory, Tyndall Air Force Base, FL, December 1989. NMERI *SS* 2.06(1)

6. Chlorine also appears to provide some degree of chemical suppression through the reactions $OH + HCl \rightarrow Cl + H_2O$ and $Cl + HO_2 \rightarrow HCl + O_2$ (Barat, R. B., Sarafim, A. F., Longwell, **J. P.,** and Bozzelli, J. W., "Inhibition of a Fuel Lean Ethylene/Air Flame in a Jet Stirred Combustor by Methyl Chloride: Experimental and Mechanistic Analysis," ***Combustor Science and Technology,*** Vol. 74, pp. 361378, 1990). However, the efficiency of the chemical inhibition reactions of chlorine appears to be much less than that afforded by bromine or iodine.