

HALON SUBSTITUTES —AN OVERVIEW

Robert E. Tapscott, Center for Global Environmental Technologies, New Mexico Engineering Research Institute, University of New Mexico, Albuquerque, NM 87131-1376, USA

ABSTRACT

Halon production will effectively end sometime this year, and, as yet, most of us are uncertain about what to put in their place. In response to this uncertainty, I want to review our options — what is available, what the drawbacks and advantages are, and what is likely to be the outcome. Before doing so, we need *to* review some definitions. We use the term ‘kubstitutes’ to mean anything that could be used in place of halon fire and explosion protection and suppression. ‘Replacements’ denote fire extinguishants that are chemically similar to the present halons; ‘alternatives,’ are everything else. ‘Chemical alternatives’ are materials such as carbon dioxide, foam, water, and dry chemical whose chemistries differ from those of the halons. ‘Engineering alternatives’ involve such approaches as rapid response and fire resistant structures.

A large number of candidate replacement agents have been announced for commercialization, and even more chemicals are under serious consideration. Yet, all of these ‘first-generation’ agents have serious tradeoffs in one way or another. Halon replacements require four characteristics: a low global environmental impact (low ODP, GWP, and atmospheric lifetime), acceptable toxicity, cleanliness/volatility, and effectiveness. Though it is very easy to find candidate replacements that meet any three of these criteria, it has been difficult to find agents that meet all four. For most (but not all) applications, at least two to three times as much of any first-generation replacement will be needed to provide the same degree of protection as provided by the present halons.

We are looking increasingly at “second-generation” agents—materials that are highly effective, yet have low global environmental impacts. Many such materials have been identified and have been shown to have low or zero ODPs and GWPs while maintaining or exceeding the effectiveness of the present halons. The problem is that we know little about manufacturability, toxicity, emissions, materials compatibility, and stability, and the market may not be sufficiently large to justify the cost of determining these unknowns.

A number of new alternatives are now under investigation. Among these are water misting systems, aerosols, and inert gases. Water misting and aerosols may allow protection while minimizing the secondary damage and the problems normally associated with water and solids. Recent advances in inert gas blends may allow the use of these agents in new applications.

However, it is obvious that there has been no breakthrough. We will have to manage our existing bank of halons carefully. Water sprinklers, dry chemicals, foams, and carbon dioxide will receive increasing use. Above all, we will have to do a better job of engineering in providing fire protection.

INTRODUCTION

This Halon Alternatives Technical Working Conference is the last to be held before halon production in the developed countries is discontinued. Recognizing this, we have directed this year's Conference, more than ever, toward the user community (Slide 1).

**HALON SUBSTITUTES -
AN OVERVIEW**

**HALON ALTERNATIVES TECHNICAL
WORKING CONFERENCE 1993**

Sheraton Old Town
Albuquerque, NM

11-13 May 1993

Robert E. Tapscott
Center for Global Environmental Technologies
New Mexico Engineering Research Institute
University of New Mexico

Slide 1

This is a momentous year for halons (Slide 2). The Fourth Meeting of the Parties to the Protocol was held in Copenhagen, Denmark on November **23-25, 1992**. At that meeting, production restrictions were added for three new groups of chemicals — HCFCs; HBFCs; and methyl bromide. Moreover, the Parties agreed to accelerate the phaseout schedule for certain controlled substances, including halons. At the Copenhagen meeting, the Parties agreed to allow for an exemption of essential uses of controlled substances **from** the consumption phaseout schedule. Specific essential-use exemptions for halons will be determined at the Fifth Meeting of the **Parties**, which is tentatively scheduled for October **15-24 1993** in Thailand. Essential-use exemptions for the remaining substances will be determined at the Sixth Meeting of the Parties to be held around September **1994**.

The Halons Technical Options Committee operating under the auspices of the United Nations Environment Programme has been reconvened, and the first meeting was held in Paris on 17-19 March. Once again, the Committee is operating under the Chairmanship of Gary Taylor and Tom Morehouse. The **1993** Committee will be preparing a report and recommendations on essential uses on a country-by-country basis for use at the fifth meeting of the Parties this fall. The next meeting of the Halons Technical Options Committee is scheduled for 6-9 July in Toronto.

The U.S. EPA has just released a preliminary announcement of their proposed rulemaking under the Significant New Alternatives Policy (SNAP) program. The proposed rule is now in press for publication in the Federal Register this month. Karen Metchis will, of course, have something to tell us about this in this session.

The National Fire Protection Association (NFPA) Technical Committee on Alternative Protection Options to Halons is concluding their work on the new NFPA Standard 2000 on Clean Agent Fire Extinguishing Systems. As you all know, Phil DiNenno, who gave the opening address at this Conference, chairs that committee.

Sometime back, the Halon Alternatives Research Corporation (HARC) did a bank management study that has now led to the imminent formation of a Halon Recycling Corporation that will facilitate halon transfer within the U.S. The Halon Recycling Corporation is expected to be formed by July. In Session 6 on bank management, will cover a recent DOD bank management study and will review an ASTM standard for Halon 1301 and some activities by the U.S. Air Force on halon management.

1992-1993 HIGHLIGHTS

- Copenhagen
- UNEP Halons Technical Options Committee
- SNAP
- **NFPA 2001**
- Halon Recycling Corporation

Slide 2

SUBSTITUTES

Today, however, I would like to focus on where we are on halon substitutes. Before doing **so**, however, we need some definitions (Slide 3). We must ensure that we are all talking about the same thing. By “substitutes” we mean anything that could be used in place of halons. ‘Replacements’ denote fire extinguishants that are chemically similar to the present halons; ‘alternatives,’ are everything else. Moreover, we often divide replacements into two types—first-generation and second-generation, loosely defined terms that I will say more about in a few minutes. ‘Chemical alternatives’ are materials such **as** carbon dioxide, foam, water, and dry chemical whose chemistries differ from those of the halons. ‘Engineering alternatives’ involve such approaches as rapid response and fire resistant structures.

DEFINITIONS

Substitutes = anything that could be used in place of halon

- Replacements = halocarbon substitutes
 - ✓ First-Generation
 - ✓ Second-Generation
- Alternatives — non-halocarbon substitutes
 - ✓ Chemical Alternatives
 - ✓ Engineering Alternatives

Slide3

REPLACEMENTS

As I mentioned, for some time, we have been talking about first- and second-generation replacements. I believe that these terms were actually introduced at the first Halon Alternatives Technical Working Conference; however, they have been loosely used (and I **am as** guilty **as** anyone about this).

Before defining first- and second-generation replacements, we need to consider two different types of agents. Physical action agents (PAAs) are those that operate primarily by heat absorption. Chemical action agents (CAAs) are those that operate primarily by chemical means—removal of flame free radicals (Slide 4).

AGENT TYPES

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

Slide 4

With this in mind, we can now define first-generation replacements as either PAAs or those **CAAs** that have high or relatively high ozone depletion potentials (**ODPs**). Second-generation agents are **CAAs** with low ODPs (Slide 5).

REPLACEMENT AGENTS

- First-Generation
 - PAAs or those CAAs with high/relatively high ODPs
- Second-Generation
 - CAAs with low **ODPs**

Slide 5

First-generation replacements refer to halocarbon candidates that we have today — those candidates that have global environmental, toxicological, or effectiveness drawbacks. Second-generation agents are those future agents that equal the halons in effectiveness, yet have acceptable global environmental and toxicological characteristics. Some might say those “mythical” future agents; however, I think that you find from this Conference that they are closer to realization than one might think.

FIRST-GENERATION REPLACEMENT AGENTS

Most of the first-generation agents are PAAs — chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs), or perfluorocarbons (FCs or PFCs) (Slide 6). The only CAAs that have been announced are hydrobromofluorocarbons (HBFCs), which have high or relatively high ODPs, and which will be phased out by 1 January 1996 under the Copenhagen amendment to the Montreal Protocol.

FIRST-GENERATION REPLACEMENTS

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

Slide 6

At this Conference, you will hear a lot about first-generation agents, since those are the only halocarbon replacements that we have today (Slide 7). There are sessions on toxicity, laboratory testing, fire suppression testing, and decomposition studies of first-generation agents.

SESSIONS ON FIRST-GENERATION AGENTS

- Session 2 - toxicity issues
- Session 3 - laboratory testing
- Session 4 - fire suppression testing
- Session 5 - decomposition studies

Slide 7

A large number of candidate replacement agents have been announced for commercialization, and even more chemicals are under serious consideration. A number of first-generation replacements have been announced for total-flooding applications (Slide 8).

ANNOUNCED FIRST-GENERATION TOTAL-FLOODING AGENTS		
FC-3-1-10	Perfluorobutane	$\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}_3$
HBFC-22B1	Bromodifluoromethane	CHF_2Br
HCFC-124	Chlorotetrafluoroethane	CHClFCF_3
HFC-125	Pentafluoroethane	CHF_2CF_3
HFC-227ea	Heptafluoropropane	$\text{CF}_3\text{CHFCF}_3$
HFC-23	Trifluoromethane	CHF_3
R-595	Blend including	HCFC-123, HCFC-22 HCFC-124

Slide 8

Until recently, the number of agents announced for streaming applications was small. Recently, however, the number has increased markedly (Slide 9).

ANNOUNCED FIRST-GENERATION STREAMING AGENTS
<ul style="list-style-type: none"> • FC-5-1-14 ($\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_3$) • HBFC-22B1 ($\text{CHBrF}_2$) • HCFC-123 ($\text{CHCl}_2\text{CF}_3$) • HCFC-124 ($\text{CH}_3\text{CHClF}$) • HCFC-227ea ($\text{CF}_3\text{CHFCF}_3$) • Halotron I (HCFC Blend) • NAF P (CFC Blend)

Slide 9

All of these first-generation agents have tradeoffs in one way or another. Halon replacements have four desirable characteristics: a low global environmental impact (low **ODP**, **GWP**, and atmospheric lifetime), acceptable toxicity, **cleanliness/volatility**, and effectiveness (Slide 10). (Some believe that manufacturability should be added *to* this list). Though it is very easy to find candidate replacements that meet any three of these criteria, it has been difficult to find agents that meet **all** four. For most (but not all) applications, at least two to three times as much of **any** first-generation replacement (except **HBFC-22B1**, which will be phased out starting 1 January 1996) is needed to provide the same degree **of** protection as provided by the present halons.

DESIRABLE CHARACTERISTICS FOR REPLACEMENTS

- Low ODP, GWP, atmospheric lifetime
- Acceptable toxicity
- Cleanliness, volatility
- Effectiveness

Slide 10

SECOND-GENERATION AGENTS

We are looking increasingly at "second-generation" agents — materials that are highly effective, yet have low global environmental impacts (Slide 11). These materials are all **CAAs**, and they all contain bromine or iodine, one or both of which appear to be necessary to have a chemically active halocarbon fire extinguishant. The important thing about second-generation agents is that despite the presence of bromine and/or iodine, they have chemical features that promote very low atmospheric lifetimes, a property that reduces the **ODPs** and **GWPs** to near zero. I am going to let others at this meeting talk about these chemical features. **Of** particular interest will be a joint paper by Ed Walters and Mario Molino on the predicted global environmental characteristics of some of these agents, and Stephanie Skaggs will be presenting **an** overview of the chemical characteristics of these agents in Session 6.

SECOND-GENERATION REPLACEMENTS

- CAAs
- Contain bromine and/or iodine
- Low atmospheric lifetimes

Slide 11

Many second-generation candidates have been identified and several have been shown to have low or zero ODPs and GWPs while maintaining or exceeding the effectiveness of the present halons. The problem is that we know little about manufacturability, toxicity, emissions, materials compatibility, and stability, and the market may not be sufficiently large to justify the cost of determining these unknowns (Slide 12).

UNKNOWNNS ABOUT SECOND-GENERATION CANDIDATES

- Manufacturability
- Toxicity
- Emissions
- Materials compatibility
- Long-term stability

Slide 12

ALTERNATIVES

More and more, non-halocarbon substitutes are being considered for replacement of halons. Already, water sprinklers are replacing halon systems in many applications. Dry chemical extinguishants and carbon dioxide are also receiving increased use. In fact, **the** Halon Alternatives Research Corporation **will** be holding a Conference specifically on alternative technologies on 11 and 12 November in Phoenix, just before the fall NFPA meeting in Phoenix.

A number of new alternatives are now under investigation (Slide 13). Among these are misting systems, particulate aerosols, and inert gas blends. Misting and particulate aerosols require decreased amounts of agents that can lead to secondary fire damage. Thus, these technologies may allow protection while minimizing the problems normally associated with water and solids. Recent advances in inert **gas** blends may allow the use of these agents in new applications, particularly in occupied areas. In setting up this conference, we have attempted a comprehensive survey of these new alternative technologies. Two sessions are scheduled on water misting systems, and entire separate sessions are scheduled for particulate aerosols and inert gases.

NEW ALTERNATIVE TECHNOLOGIES UNDER INVESTIGATION

- Misting
- Particulate aerosols
- Inert gas blends

Slide 13

CONCLUSIONS

There are no breakthroughs, no clear-cut winners, no all-encompassing solutions (Slide 14). Perhaps someday there will be a "son of wonder gas," but right now it does not exist. We will have to manage our existing bank of halons carefully. Water sprinklers, dry chemicals, foams, and carbon dioxide will receive increasing use. Above all, we will have to do a better job of engineering in providing fire protection.

CONCLUSIONS

- No breakthroughs, no clear-cut winners, no all encompassing solutions
- Halon bank management will continue to be important
- Water, dry chemicals, foams, carbon dioxide will increase in use
- Proper fire protection engineering will be more important than ever

Slide 14