RECENT ADVANCES IN DEVELOPMENT OF NON-VOLATILE PRECURSORS [NVPs] TO ALTERNATIVE HALON FIRE EXTINGUISHING AGENTS WITH REDUCED GLOBAL ENVIRONMENTAL IMPACTS

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ABSTRACT

Our group has now prepared NVP agents which have proved to be capable of generating highly effective HBFC and olefinic bromofluorocarbon extinguishing agents when heated at moderately high temperatures as would be encountered in proximity to typical fire zones. The first NVP agents proved to be as effective in fire extinguishing capabilities as the most efficient Halon agents now in use. NVP agents would be predicted to have no ozone depletion, global warming, or toxic vapor problems due to emissions to the atmosphere as a result of fire extinguishing operations, tank leakages or similar sources of accidental releases. NVP agent requirements for firefighting operations should be greatly reduced in comparison to conventional volatile Halon or alternative agents, most of which evaporate en route to the fire when delivered as fire extinguishing agents. The liquid streaming characteristics of non-volatile agents should result in extended throw ranges, with increased safety for firefighting personnel, since NVP agents can be projected from much greater distances. Agent requirements would be very considerably reduced also as a result of reduced losses due to evaporative effects. To address concerns about possible environmental contamination by use of these non-volatile agents, preliminary research indicates that the NVPs thus far investigated would be susceptible to gradual hydrolysis to yield relatively inoccuous materials. Research on several new promising NVP agents will be reported.

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Chlorofluorocarbon (CFC) emissions pose serious environmental problems in terms of unacceptably high stratospheric ozone depletion potentials (ODPs); ozone protects life forms from damaging ultraviolet radiation. CFCs are used as refrigerants, solvents, foam-blowing agents, and aerosol propellants. Halons are very efficient bromofluorocarbon (BFC) fire extinguishing agents, chemically related to CFCs; also with seriously high ODPs and unacceptably high global warming potentials (GWPs). (These compounds are very volatile, with high chemical stabilities, so they pass unscathed through lower atmospheric levels to accumulate in the stratosphere. In lower atmospheric regions these agents prevent passage of infrared radiation from the earth, thus creating the global warming. In stratospheric regions in which agents finally accumulate, the highly energetic UV radiation from the sun is able to overcome the chemical stabilities of these CFC and BFC agents, causing formation of ozone destroying free radical species which arise from W degradation of these compounds.) Halons account for 15% of the total ODP problem. Regulatory commissions such as the EPA have called for cooperative efforts to stem the rate of emissions and to seek effective alternative firefighting agents. (1-7)

Since the poor deliverability and requirements for excessive dose, and high ODP, GWP and vapor toxicity problems are all due to the high volatility of Halons, we proposed a new approach, with use of NVP firefighting agents which would degrade in the heat of fire to release analogs of conventional Halons. In this first phase of project work we synthesized five new compounds which decompose thermally in accordance with the following schemes:

$CFBr_2CO_2CH_2CH_3 \xrightarrow[\text{fire zone}]{\text{heat from}} CFBr_2H + CH_2{=}CH_2 + CO_2$

Ethyl Dibromofluoroacetate ["EBDFA"]

$CF_2BrCO_2CH_2CH_3 \xrightarrow[\text{fire zone}]{\text{heat from}} CF_2BrH + CH_2{=}CH_2 + CO_2$

Ethyl Bromodifluoroacetate ["EBDFA'] (FM-100)

$Br{-}CH_2{-}CH_2{-}CH(Br){-}CH_3 \xrightarrow[\text{fire zone}]{\text{heat from}} 2\ HBr + CH_2{=}CH{-}CH{=}CH_2$

1,4-Dibromobutane ["DBB"]

$I{-}CH_2{-}CH_2{-}CH(Br){-}CH_3 \xrightarrow[\text{fire zone}]{\text{heat from}} HBr + HI + CH_2{=}CH{-}CH{=}CH_2$

1-Iodo-3-bromobutane ["IBB"]

$CF_2Br{-}CHFBr \xrightarrow[\text{fire zone}]{\text{heat from}}$ (undetermined pyrolysis products)

1,2-Dibromo-1,1,2-trifluoroethane ["DBTFE"]

These compounds were tested for fire extinguishing efficiency at the Fire Research Labs of the US Air Force at Tyndall Air Force Base, Florida [TAFB]. The agents cited in the following table are the first NVP halon-like compounds ever to be tested for possible use as fire extinguishing agents. It is therefore particularly noteworthy that all agents worked very well indeed. In fact, most proved to be superior to any of the halons currently in use throughout the world, or any of the alternative agents currently proposed as replacements for the current Halons (which are being phased out as a consequence of the Montreal Protocol on Substances That Deplete the Ozone Layer).

PROPERTIES OF FIRE SUPPRESSION AGENTS
(TESTS PERFORMED AT TYNDALL AFB, FL [TAFB])

	AGENT	FORMULA	MW	B.P. °C	TAFB CUP BURNER %
**	1301	CF_3Br	149	- 72	1.3 •
**	1211	CF_2BrCl	165	- 4	1.4
***	FM-101	CF_2HBr	131	- 16	1.4 •
***	C6	C_6F_{14}	338	60	2.0
****	EBDFA	$CF_2BrCO_2C_2H_5$	203	170	2.2
****	*EDBFA	$CFBr_2CO_2C_2H_5$	264	190	1.0
****	DBB	$BrCH_2CH_2CHBrCH_3$	216	175	7.9
****	IBB	$ICH_2CH_2CHBrCH_3$	263	220	4.0 •
****	DBTFE	$CF_2Br\text{-}CHFBr$	242	76	1.8

• Estimated values
** Currently most widely used Halon agents
*** Alternative agents being proposed for replacement of Halons
**** NVP candidates submitted for testing

NOTE: "TAFB Cup Burner %" values are minimum percentages concentration in air of the extinguishing agent required for extinguishment of a flame in the cup burner apparatus. Low percentage values denote greater fire extinguishing capabilities; thus, the agent "EDBFA" is currently the most effective fire extinguishing agent of any Halon or alternative Halon tested in this extensive program.

Although DBB and IBB are shown to be somewhat less effective than the conventional Halons, these agents are potentially very cheap and, since much less of these agents would be required for adequate extdinguishment (due to the low volatility and loss loss due to evaporation en route to the fire) these would appear to be actually much more effective than the conventional Halons. It can be noted in the table that not only are these agents very highly effective fire extinguishing agents, these are also indeed truly non-volatile agents which would therefore pose essentially no environmental vapor threat in terms of ozone depletion at stratospheric altitudes, global warming effect at any altitude, or vapor hazard to exposed firefighting or other personnel in close proximity to a fire zone in which such agents would be used. Moreover, since the NVP agents are non-volatile, there should exist much lower requirements for use of such agents in firefighting operations: with the highly volatile Halon or alternative Halon agents, most of the agent is lost by evaporation en route from the delivery source to the fire, and therefore excessively high quantities must be delivered to ensure adequate concentrations in the fire zone itself. Further, since non-volatile agents can be streamed in delivery to a fire for much greater distances, this would represent a significantly increased safety factor for firefighters who could therefore stand at much greater distances from dangerous fires.

To address concerns which may arise concerning environmental contamination by use of these non-volatile agents, preliminary research by this group indicates that both EBDFA and EDBFA agents would be susceptible to hydrolysis to yield relatively innocuous materials. Thus, for agent EDBFA, the course of hydrolysis appears to be:

$$CFBr_2-C(=O)-O-CH_2-CH_3 \xrightarrow[\text{ambient conditions}]{H_2O} HO-C(=O)-C(=O)-OH + HBr + HF + CH_3CH_2OH$$

oxalic acid

(The other NVP agents appear to follow similar pathways to form relatively non-innocuous compounds.)

The pyrolysis of a NVP provides considerable superiority over current Halon agents. Thus, the non-volatility of the precursor would provide many important and unique advantages:

1. The high ODPs and GWPs of the volatile Halons are associated with their high stabilities. In searching for Halon alternatives the approach thus far has been directed to HCFCs (CFCs with one or more hydrogen atoms which significantly reduce chemical stability for these agents) with the hope that the HCFCs would not survive ascent into the stratosphere. Unfortunately, the chemical stabilities are great enough to continue to pose significant ODP problems: it is unlikely that regulatory commissions will permit use of HCFCs beyond the year 2000 for any purpose, including fire extinguishment. (9)

A NVP (which would thermally degrade in the heat of a fire to form a Halon extinguishing agent) provides a new approach to ODP and GWP problems. The non-volatile NVP would not acculumlate at any atmospheric level: hence, there would be no GWP or ODP concerns.

2. Recent evidence shows HCFCs to be unacceptably toxic and mutagenic. (10) This poses serious problems for firefighters who would often be exposed to such materials. NVP/OBFC agents would have essentially no vapor hazard.

3. Highly volatile Halons and HCFCs have very limited range of delivery when directed onto fires from pressurized hoses: more than 90% of the agent vaporizes en route to the fire and is lost without effect, with serious toxicity, ODP, GWP and expense considerations. Moreover, firefighters must apply these volatile agents at very close range to the fire, with great hazards due to flame and possible explosion effects. The excellent streaming effects of the proposed liquid NVP agents provide drastically reduced agent requirements, and greatly increased range for delivery onto fires.

4. HCFCs currently being tested for use as extinguishing agents <u>may themselves be dangerously flammable under conditions of *high* heat</u>. (11) Although this may also be true for NVPs, the danger would be considerably less. Thus, Halons and HCFCs are so volatile that these must be applied in very large excess to ensure adequate concentrations in fire zones; but delivery requirements for NVP agents would be very much smaller. Hence, such anomalous flammability problems as might conceivably develop would be minimized for the NVP agents.

5. After extinguishment there would be residual NVP agent still pyrolyzing to Halon agents due to hot surface contacts. This should serve to prevent flash back fire effects which frequently arise after initial extinguishment.

SIGNIFICANCE OF RESULTS

This study may establish an important direction for future development of effective non-volatile Halon fire extinguishing agents with minimal hazards to the environment and firefighting personnel. Such non-volatile Halon precursors could be formulated for use in firefighting foam formulations for large scale petroleum and petrochemical fire fighting applications, and also in paints, resins, or other coating materials. In all applications, there would be little or no emissions to the atmosphere due to fire extinguishing operations, or to tank leakages, inadvertent valve openings, and similar sources of accidental releases which currently pose enormous environmental problems. NVP agents would be as "clean" as AFFF formulations: there is no residue from heat or combustion. Use requirements and toxicities for NVP agents may be drastically reduced relative to Halons or HCFCs. Extended throw ranges for these non-volatile agents should result in greatly increased safety for firefighting personnel who could thereby direct these extinguishing agents at much greater distances from the fire.

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