

**THE MASSACHUSETTS
TOXICS USE REDUCTION INSTITUTE**

**ALTERNATIVE FIRE
EXTINGUISHING AGENTS:**

**Non-Volatile Precursors to
Olefinic Bromofluorocarbons**

FINAL REPORT

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University of Massachusetts Lowell

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Non - Volatile Precursors to Olefinic Bromofluorocarbons

FINAL REPORT

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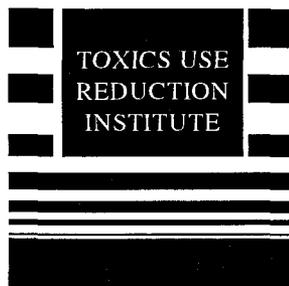
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The 1993-1994 Toxics Use Reduction Research Fellows Program

The Toxics Use Reduction Institute
University of Massachusetts Lowell

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Toxics Use Reduction Institute Research Fellows Program

In 1991, the Toxics Use Reduction Institute established the Research Fellows Program at the University of Massachusetts Lowell (UML). The Research Fellows Program funds toxics use reduction projects performed by a graduate student and his/her advisor. The goals of the Research Fellows Program are:

- to develop technologies, materials, processes, and methods for implementing toxics use reduction techniques
- to develop an understanding of toxics-use-reduction among UML graduate students and faculty
- to facilitate the integration of the concept of toxics use reduction into UML research projects
- to provide UML faculty with "incubator" funding for toxics use reduction related research, and
- to act as a liaison between Massachusetts industries and UML faculty.

Notice

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ABSTRACT

Our group has prepared many non-volatile precursor (NVP) agents which have been shown to generate hydrobromofluorocarbon and olefinic bromofluorocarbon fire extinguishing agents when heated to temperatures typical of those encountered near a fire zone. The liquid NVP agents proved to be as effective as the most efficient Halon agents now in use. Solid polymer NVP agents are now being prepared for possible use in the prevention of fires in small enclosed areas. All NVP agents show greatly reduced emissions to the atmosphere, and would be predicted to have no ozone depletion, global warming or toxic vapor problems. Lower vapor pressures in the case of liquid NVP agents results in less of the agent evaporating en route to the fire zone. In addition, the greater streaming characteristics of the liquid NVP agents greatly reduces the agent requirements and increases the throw ranges, which results in increased safety for firefighting personnel. Solid NVP agents would have zero vapor pressure and thus no loss to the atmosphere due to evaporation. The chemical nature of all of the NVP agents prepared so far suggests that gradual hydrolysis to yield relatively innocuous materials would prevent extended environmental contamination.

PROJECT DESCRIPTION

Bromofluorocarbons, used in Halon fire extinguishing agents, have been shown to cause ozone depletion, global warming, and toxic vapor problems due to the high volatility of these agents. In order to extinguish a fire from a distance using a hose, a tremendous amount of gaseous Halon agent is required since more than 90% of the agent evaporates into the atmosphere before ever reaching the fire. In the lower regions of the atmosphere these agents prevent infrared radiation from escaping, causing global warming; in stratospheric regions, where the agents finally accumulate, the highly energetic ultraviolet radiation from the sun causes formation of free radical species which destroy ozone. Halons account for 15% of the total ozone depletion potential (ODP) problem. Both international and United States law mandate the phase-out of Halons. (1-6)

While conventional Halon agents are excellent for small enclosed areas, they are simply not practical for other types of fires, such as ordnance fires, where the agent must be delivered from a distance. Halons are currently not suitable for use in these types of fires. In addition to the global warming problem, the toxicity of these agents is a danger to fire-fighting personnel.

Objectives. Since it is primarily the high volatility of these agents which causes their poor deliverability and vapor toxicity problems, we conceived of the use of non-volatile materials which would break down into Halon-like firefighting agents in the heat of the fire zone. The first non-volatile precursors (NVPs) we examined were liquid at ambient temperatures, and therefore would have greater streaming characteristics and lower vapor pressures than gaseous Halons. Thus, loss to the atmosphere would be greatly reduced. The first NVP agents developed here at UMass-Lowell proved to be as effective in fire extinguishing capabilities as the most efficient Halon agents currently in use. These liquid agents were of probable high toxicity, but were chosen in view of their ease of synthesis or accessibility, as well as the ease of determination of fire extinguishing capabilities in a conventional cup-burner apparatus. The emphasis is now shifting towards solid NVP agents which would act as fire prevention agents. These solid agents are based on the liquid agents studied previously. Although the liquid monomers are expected to be toxic, it is anticipated that the solid polymers would be non-toxic, as is the case with most polymer systems.

RESEARCH METHODOLOGY

This work involves conventional organic syntheses and testing of the resulting NVP agents in conventional test assemblies at Tyndall Air Force Base, Florida. A test assembly for solid NVP agents is being developed.

ENVIRONMENTAL IMPACTS AND TOXICS USE REDUCTION IMPLICATIONS

Emissions to Air. The greatest advantage of non-volatile firefighting materials is the reduced loss to the atmosphere of the agent due to evaporation. All of the NVP agents prepared have had very low volatility, or no volatility in the case of solid agents. In addition to less material being lost to the atmosphere, less is needed in the first place since most of the agent would reach the fire zone compared to only about 10% of volatile Halon agents. Thus, the required amount of agent to extinguish a fire is greatly reduced. For example, if we assume that 10 pounds of Halon agent is needed to put out a fire, then less than 1 pound of the NVP agent would work as well. This is assuming that both agents have the same fire extinguishing efficiency; some of the NVP agents appear to be better than conventional Halon agents. Loss of agent due to accidents such as leaks results in very little, if any, material escaping into the atmosphere.

Ground and Water Contamination. Contamination on the ground presents a different problem. Preliminary research suggests that liquid NVP agents would gradually hydrolyze at ambient temperatures. However, the products of hydrolysis are not specifically known. It does appear that compounds such as oxalic acid, hydrobromic acid and hydrofluoric acid would be formed, but would not be expected to persist in the environment. The polymeric NVPs are totally insoluble in water, but more data is needed to determine what problems may arise due to the physical presence of these materials in the environment. More data is needed in this area to make a determination on the impact to the ground environment.

Toxicities. In regard to toxicity of these agents more data is needed. It should be noted, however, that the toxicities of the polymer NVP agents are expected to be extremely low. Polymerization of many toxic monomers, such as styrene, tetrafluoroethylene, and vinylidene chloride, renders them benign (7). Toxicities of feedstock starting materials will present the same concerns as exists for toxicities of many monomers currently used in the production of polymeric materials. In addition, the solid NVPs are much more efficient, pound for pound, than gaseous Halon; therefore, the requirements for use, and thus the requirements for production, will be significantly reduced.

POTENTIAL COMMERCIAL APPLICATIONS

The Air Force and several other agencies have expressed considerable interest in further development of this work and have promised significant funding for further research efforts. Potential incorporation of these NVP agents into a variety of firefighting and fire prevention formulations is very significant. The NVP agents could be introduced into a stream of water, for example, and used to fight an ordnance fire. The solid, polymeric NVP agents could be used to coat and protect

materials such as electronic equipment, munitions containers, etc.

RESEARCH RESULTS

The following agents have been prepared and have been or will be tested at the Fire Research Laboratories of the US Air Force at Tyndall Air Force Base, Florida [TAFB], as indicated.

Agent		MW(g/mole)	B.P.(°C)	CB%
Vinylidene Bromide	$\text{CH}_2=\text{CBr}_2$	186	92	NA
3,3,4,4-Tetrabromo-1,4-butanediol	$\text{HO}-\text{CH}_2-\text{CBr}_2-\text{CBr}_2-\text{CH}_2-\text{OH}$	406	solid	NA
3-Bromo-1-iodobutane	$\text{I}-\text{CH}_2-\text{CH}_2-\text{CHBr}-\text{CH}_3$	263	220	4.0
1,2-Dibromo-1,1,2-trifluoroethane	$\text{CF}_2\text{Br}-\text{CHFBr}$	242	76	1.8

Note: Lower cup burner results indicate increased fire extinguishing capabilities; few Halon agents have values below 2.0.

The following solid agents are expected to have no toxicity:

Polyvinylidene Bromide $\{\text{CH}_2-\text{CBr}_2\}_n$

Polyvinyl Bromide $\{\text{CH}_2-\text{CHBr}\}_n$

As yet the solid NVP candidates have not been evaluated for fire extinguishing capabilities. A method for determining the "cup burner %" for solid materials is being developed. The test used for fire retardent materials is not appropriate.

CONCLUSIONS

The NVP agent candidates which have been tested have shown that the goal of this research is being reached. Successful Halon replacements with reduced ozone depletion potentials and global warming potentials have been prepared and tested, although toxicities still need to be evaluated. Many of these replacements have been proven to be more effective than currently used Halon agents. Furthermore, it has been shown that solid NVP agents, likely with no ozone depletion and global warming potentials, can be easily prepared.

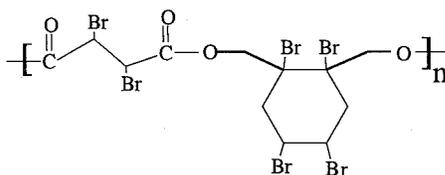
DIRECTION FOR FURTHER RESEARCH

Toxicity and other environmental studies will be important for future NVP research.

Development of solid NVP agents is very important. Specific characteristics of the different polymeric agents need to be evaluated. This includes establishing cup-burner type percentage data which is comparable to the liquid NVP agent data.

Other possible solid agents include:

"PolyTBBDO Carbonate" $[-\text{CH}_2\text{-CBr}_2\text{-CBr}_2\text{-CH}_2\text{-O-CO-O-}]_n$ and



Scale up of all the NVP candidates needs to be studied in terms of cost, efficiency, and environmental health and safety impacts. This has been and will continue to be the integrated theme of our research. We are proud that this TURI supported work has led to \$360,000 from the Air Force for continuation of this research.

ACKNOWLEDGMENTS

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