

LOW VOLATILITY HALON FIRE EXTINGUISHING AGENTS

WITH REDUCED GLOBAL ENVIRONMENTAL IMPACTS

William W. Bannister, David W. McCarthy,
Arthur Watterson, and John Patronick
John R. Floden, Consultant
Department of Chemistry
University of Massachusetts at Lowell
Lowell, Massachusetts 01854; [508] 934-3682

Robert Tetla, Captain, USAF
Wright Laboratories, Fire Research Division (WL/FIVCF)
Tyndall AFB, FL 32403-6001

Program Manager: Dr. Frederick Hedberg
Air Force Office of Scientific Research
Bolling AFB, DC

ABSTRACT

The continuation of work on non-volatile precursors (NVPs), which pyrolyze in the heat of a fire to generate Halon-like fire extinguishing agents, will be discussed. Both chemical and physical modifications of existing Halon or Halon alternative agents are being studied. From the chemical standpoint, syntheses of new polyolefinic fluorobromocarbons and brominated polyolefins polyesters have been attempted. One of these (polyfluorotribromoethylene, PFTBE) appears particularly promising, and investigations are being pursued on several other candidates.

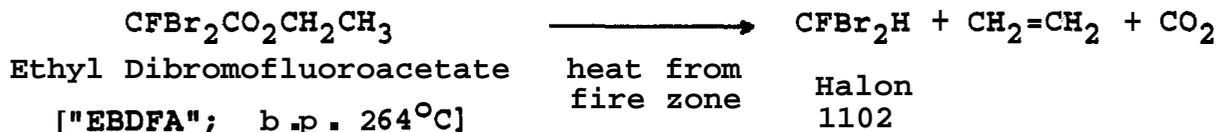
In terms of physical modifications, high volatility conventional and alternative Halons can also be gelled using a variety of highly effective gelants to form relatively non-volatile formulations.

NVP agents have greatly reduced ODP, GWP and toxic vapor properties, and pose greatly reduced atmospheric emissions due to fire extinguishing operations or from accidental releases. Agent requirements for firefighting operations would be greatly reduced, in comparison to conventional agents, most of which evaporate en route to a fire when delivered as streaming agents. Greatly extended throw ranges would result in increased safety for firefighters, since NVP agents can be projected from much greater distances.

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Within the past few years there has been much attention directed to possible drop-in replacements for Halon fire extinguishing agents which are now no longer in production, due to their unacceptable ozone depletion and global warming potentials [ODP, GWP]. Large stockpiles of Halons 1211 (CF₂BrCl; b.p. -2.5°C), 1301 (CF₃Br; b.p. -58°C), and to a lesser extent 2402 (CF₂BrCF₂Br, b.p. 47°C) are still maintained in the Halon bank, however, for future use on a prioritized basis for firefighting requirements. For total flood agent systems, one of the most promising high volatility candidates is trifluoromethyl iodide (CF₃I, b.p. = -22°C). For streaming and similar agent compositions which require lower volatilities, a variety of fluorocarbon (e.g., C₆F₁₄, b.p. 60°C) and hydrochlorofluorocarbon (e.g., HCFC 123 (CF₃CHCl₂; b.p. = 27°C)) compositions have been tested and marketed. For streaming agent applications even the higher boiling of these compositions are still sufficiently volatile that very large amounts of such agents need to be delivered to a fire in order to ensure adequate extinguishing concentrations; most of the agent is lost in delivery to the fire zone. None of these agents enjoys the low toxicities provided by the Halons; and, particularly for the HCFC agent systems, moderate but probably eventually unacceptable ODP and GWP parameters pertain.

Since the poor deliverability and requirements for excessive dose delivery, and the high ODP, GWP and vapor toxicity problems are all due to the moderate to high volatilities of these compounds, we initiated an investigation of non-volatile precursor (NVP) fire-fighting agents which would degrade in the heat of fire to release analogs of conventional Halons. The first phase of project work, completed two years ago, involved the synthesis and study of several new compounds which decompose thermally to yield olefinic and hydrobromofluorocarbon (OBFC, HBFC) products. For example:



The compounds were tested for fire extinguishing efficiency at the US Air Force Wright Laboratories Fire Research Division at Tyndall Air Force Base, Florida [TAFB]. All of the compounds had good cup burner extinguishing values; two of the agents (including "EBDA", above) were actually superior in fire extinguishing performance to the Halons.

Moreover, since much less of these agents would be required for adequate extinguishment (due to the low volatility and loss due to evaporation en route to the fire) these would appear to be actually even more effective than the conventional Halons.

The compounds which were initially investigated were all liquid species of fairly simple molecular structure. The entire thrust of this study was to ascertain the general feasibility of thermal cracking of large molecules to afford gaseous Halon-like extinguishing agents in the heat of a fire. Although no toxicity studies were performed, it was understood that all of the initial agents would be unacceptably toxic, particularly in terms of ingestion or absorption through the skin. Having demonstrated, however, the general feasibility of this approach, attention was directed in the current research program to development of NVP fire extinguishing agents which would be safe, cheap and efficient. Such NVP agents would have greatly reduced ODP, GWP and toxic vapor properties, and would pose greatly reduced atmospheric emissions due to fire extinguishing operations or from accidental releases. Agent requirements for firefighting operations would be greatly reduced, in comparison to conventional agents, most of which evaporate en route to a fire when delivered as streaming agents. Greatly extended throw ranges would result in increased safety for firefighters, since NVP agents can be projected from much greater distances.

Two approaches are being adopted in this study:

1. Chemical modifications of existing Halon or Halon alternative agents are being studied. From the chemical standpoint, syntheses of new polyolefinic bromo- and fluorobromocarbons and of similar polyesters, have been attempted.
2. Physical modifications of existing high volatility Halons or alternatives are also being studied. These include gelation (using a variety of highly effective gelants to form relatively non-volatile formulations); and encapsulation under pressure in expandable polymeric microspheres for delivery to a fire.

SUMMARY OF CURRENT RESEARCH EFFORTS

1. Chemical modifications of Halon or Halon alternatives.

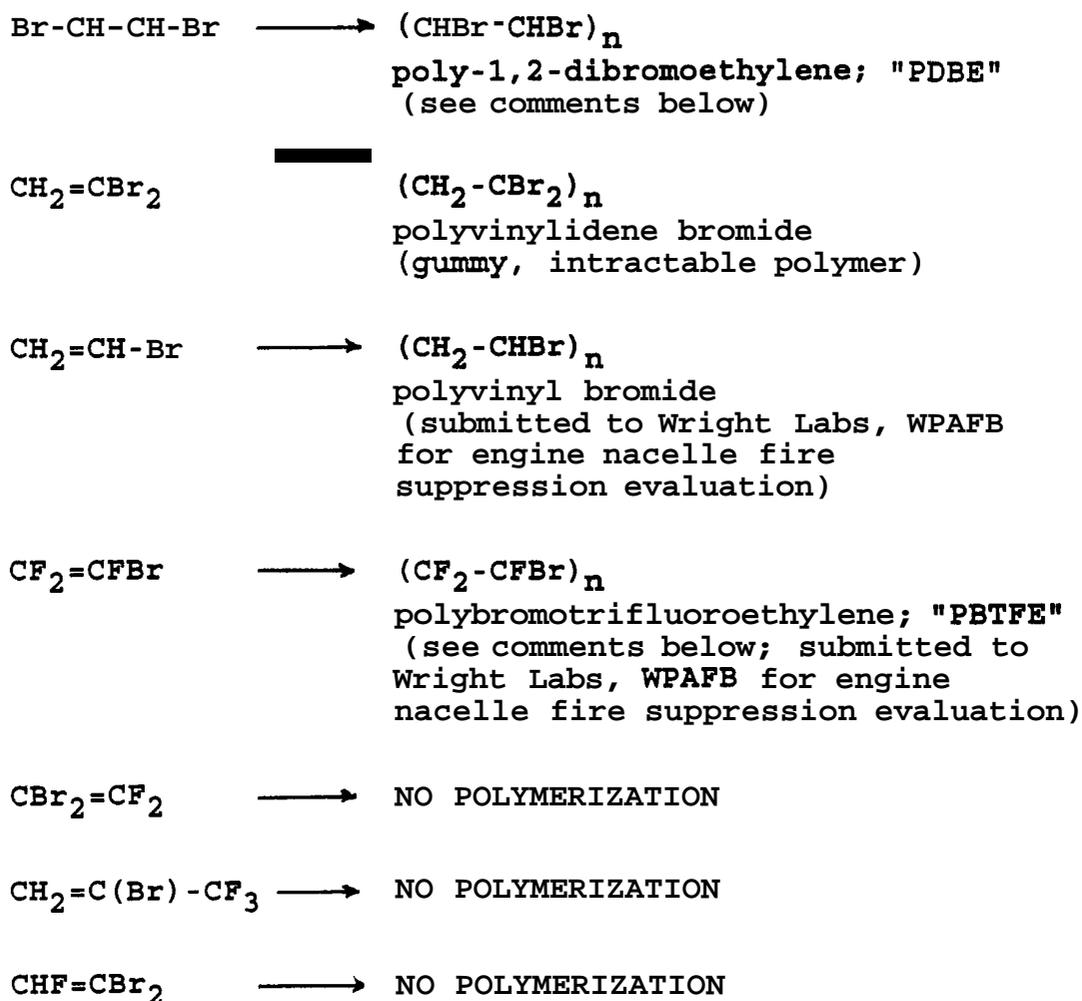
From the chemical standpoint, syntheses of new polyolefinic bromo- and fluorobromocarbons and of similar polyesters, have been attempted.

A. Addition polymerizations and reactions.

These have all been performed using free radical initiation conditions, involving gamma radiation (0.1; 0.5; 1.0; and 2.0 megarad doses) in the UMASS-Lowell nuclear reactor; and aqueous emulsification polymerization with surfactant and lauroyl peroxide initiation.

None of the gamma irradiation experiments were successful; all of these resulted in extensive debromination. No further gamma irradiation experiments are now contemplated, for this reason.

As noted below, polymerizations of three monomers were observed; another (polyvinyl bromide) was purchased. It is planned to undertake solution polymerizations of all the monomers using 1,1'-azobis(cyclohexane)carbonitrile as an initiator.



(Solution polymerization is also contemplated for 4-bromo-3-chloro-1-butene $[\text{CH}_2=\text{CH}-\text{CH}(\text{Cl})-\text{CF}_2\text{Br}]$. This monomer has previously had been demonstrated by this group to be an extremely efficient fire extinguishing agent.)

COMMENTS ON POLYOLEFINS

Of the four polymers which were obtained, polyvinylidene bromide proved too intractable as a gummy polymer for further work in this form. Our entire lot of polyvinylbromide was submitted for evaluation to Wright Laboratories for evaluation in engine nacelle fire suppression tests; more of this polymer will be synthesized, although it is not anticipated that this will prove to be a highly effective extinguishing agent in view of its low bromine content.

Thermal gravimetric analysis (TGA) was performed on both polydibromoethylene (PDBE) and polybromotrifluoroethylene (PBTFE) to ascertain extent and character of thermal depolymerization. As can be seen in Figure 1, the non-fluorinated polymer did not pyrolyze cleanly at all, and a large amount of char remained at the end of the cracking process.

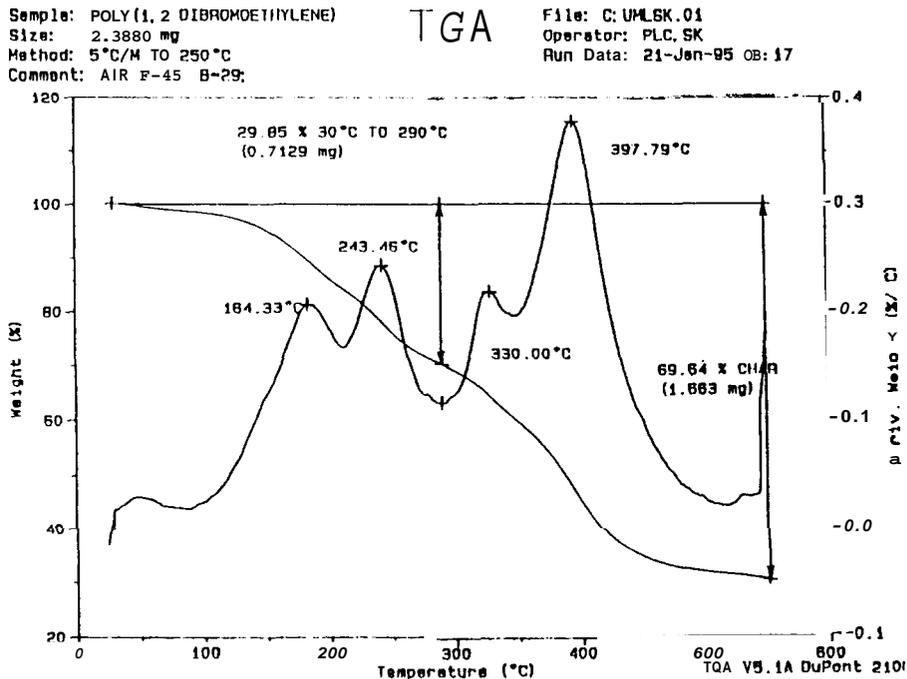


Figure 1. Pyrolysis of Polydibromoethylene ("PDBE")

For polybromotrifluoroethylene ("PBTFE") the pyrolysis was much cleaner, as can be seen in Figure 2:

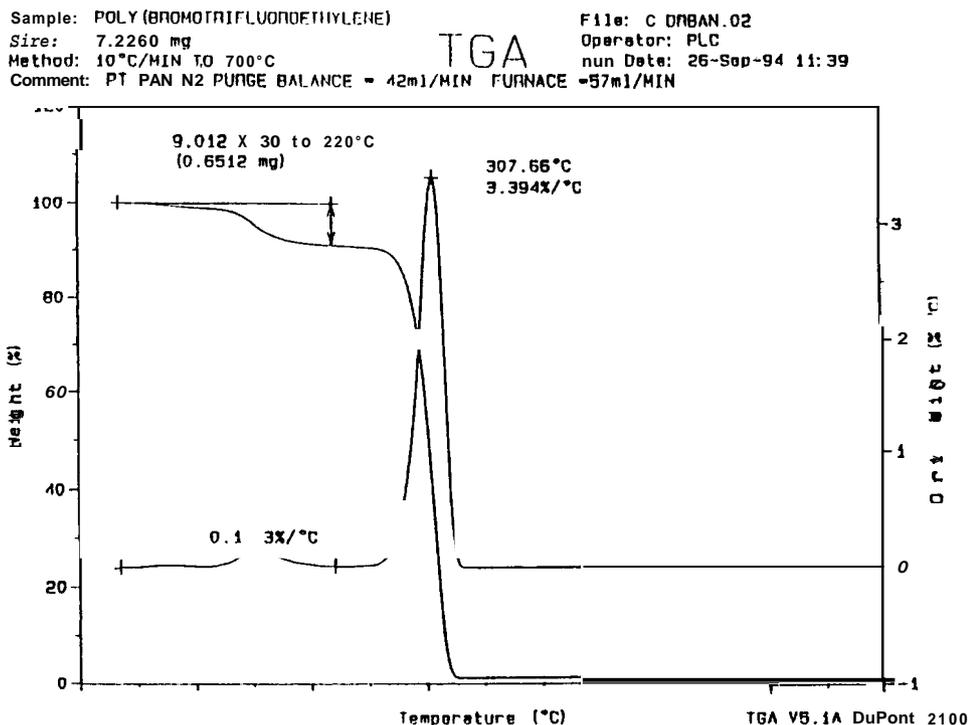


Figure 2. Pyrolysis of Polybromotrifluoroethylene ("PBTFE")

With this fluorinated polymer, the cracking is complete (there is no significant char or other residue). Cracking occurs almost entirely at about 300°C (about 550° F); some small amount of pyrolysis is observed above 150°C, but this may be due to absorbed water (water vapor was observed in the infrared spectrum; the cracking product was identified as the monomeric bromotrifluoroethylene building block, on the basis of the infrared spectrum). These conditions indicate reasonably high shelf stability at ambient temperatures and an ability to degrade at low fire temperatures.

In the case of the non-fluorinated polydibromoethylene ("PDBE", Figure 1), there appear to be a large number of independent cracking processes with no probability for a completely irreversibility. On the other hand, it appears possible that the facile thermal degradation of the fluorinated polytrifluorobromoethylene ("PTFBE", Figure 2) could be attributed to a low energy of activation for a readily reversible polymerization process. It is known that the monomeric bromotrifluoroethylene very easily and spontaneously pdpolymerizes, indicating a low energy of activation for this process. The retropolymerization should share the same energy

of activation; hence the ease of depolymerization. It is then tempting to speculate that fluorine substitution facilitates cracking processes in general; see Figure 3. This would substantiate an earlier observation by Dr. Robert Tapscott at NMERI that fluoro groups are beneficial in fire extinguishing compositions.

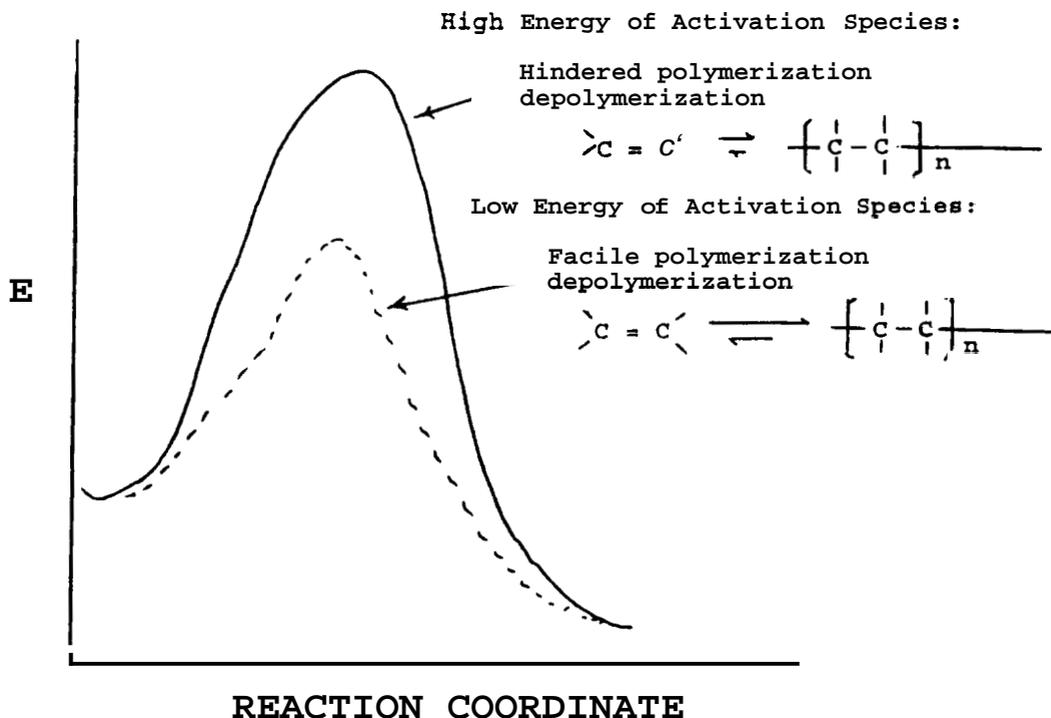


Figure 3. Postulated reaction coordinate diagram for PBTFE.

From the standpoint of determination of fire extinguishing capabilities, no good analog of the cup burner testing apparatus developed at NMERI and elsewhere exists for solid NVP agents. The monomeric bromotrifluoroethylene which was identified as being the sole product of cracking of PBTFE was tested using the NMERI cup burner apparatus at Tyndall AFB, with a value of about 5.5 being observed (as compared with values of about 3 for the Halons and for CF_3I ; and about 5.5 for HCFC 125).

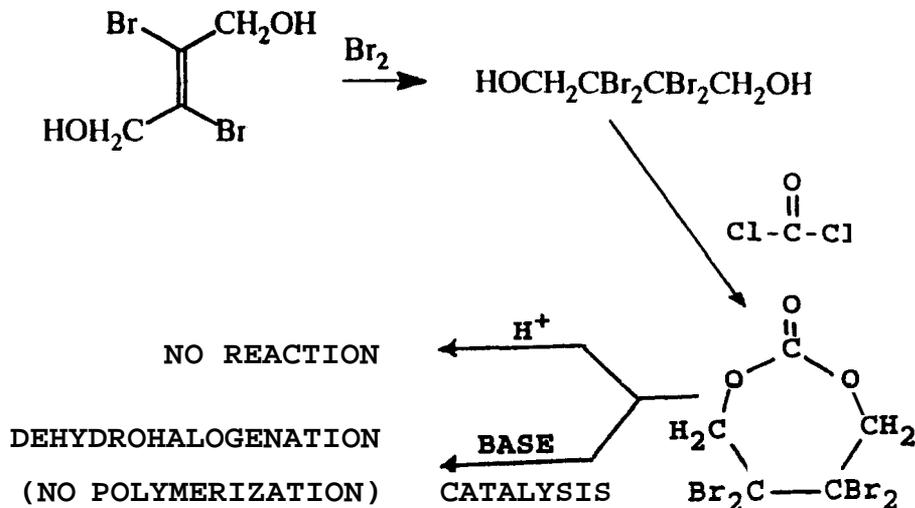
In preliminary "waste basket" fire extinguishment testae, PBTFE proved effective in extinguishment. Comparison testing with other agents was not performed, however.

Preliminary toxicity testing was performed over a five week period, using gold fish in 1.5 liters of water in which 50

mg of PBTFE had been suspended. No deleterious effects on the fish were noted.

B. Brominated polyesters.

Polymerization to form a polycarbonate was attempted using phosgene (as triphosgene precursor) with 2,2,3,3-tetrabromo-1,4-butanediol. A cyclic carbonate was readily formed; polymerization of this carbonate ester was attempted using acid catalysis (with no results) and base catalysis (resulting in extensive dehydrohalogenation).



An attempt will be made to prepare the corresponding polyoxalate, using oxalyl chloride instead of phosgene. The eight-membered ring which would result if cyclization were to occur would be much less favored than the seven-membered ring observed with the carbonate system; hence polymerization is anticipated to be a more favored process for the oxalate.

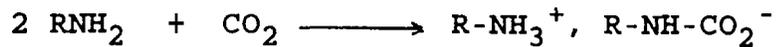
2. Physical modifications of existing high volatility Halons.

Physical modifications of existing high volatility Halons or alternatives are also being studied. These include gelation (using a variety of highly effective gelants to form relatively non-volatile formulations); or encapsulation under pressure in expandable polymeric microspheres for delivery to a fire.

A. Amine gelling agents.

Small amounts of cheap, low toxicity amines such as cyclododelyamine ("CDDN"), dehydroabietylamine ("Amine D"), and

other commercially available amines dissolve easily, completely and quickly into Halon and similar halogenated extinguishing formulations. Upon addition of very small amounts of carbon dioxide, carbamate formation and gelation of the solution occur practically immediately:

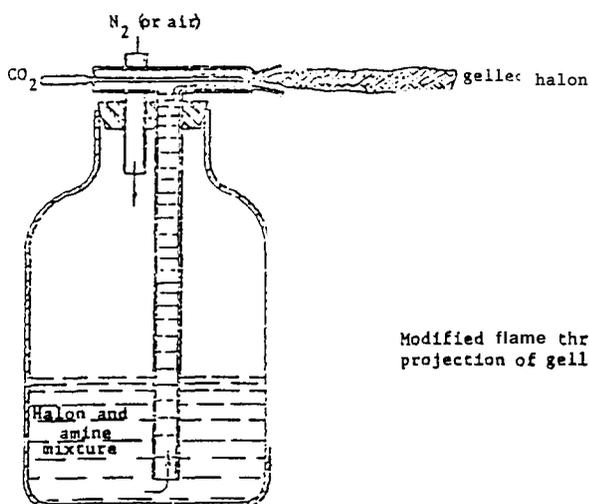


e.g., R = cyclododecyl for CDDN

(Small amounts of water facilitate the process.) The process is applicable to any Halon system, providing very greatly enhanced deliverability to a fire. Moreover, volatilities of the Halons are drastically reduced, thus practically eliminating any evaporation en route to the fire (during which time ungelled volatile Halons will almost completely evaporate, requiring very large excess of agent in order to achieve adequate extinguishing concentration at the fire zone itself).

In a recent test with Halon 1211 (b.p. -2.5°C) a solution was prepared at -10°C with components as indicated below. After carbonation with 2 g of Dry Ice, gelation occurred upon warming to just above 0° . After warming to 20° and standing in an open beaker for another 10 minutes, and then subsequently for 24 hours, the compositions were determined to be as indicated also below.

	INITIAL	10 MINUTES	24 HOURS
Halon 1211	40 g	21 g	16 g
CDDN	2.5 g	2.5 g	2.5 g
Nujol mineral oil	11.5 g	11.5 g	11.5 g
Water	1 g	1 g	1 g



Modified flame thrower for projection of gelled halon

The gel is a thick grease, which can easily be projected long distances from a modified flamethrower as shown in Figure 4. Alternatively, the gelation process can be accomplished by introduction of the components into a fire hose and projected with a long distance stream with the gelled Halon held in the water, from the hose nozzle.

(Naturally, ungelled Halon 1211 would have completely evaporated within a minute at 20°C .)

Figure 4.

On heating in a fire zone, the gelled Halon readily liberates the extinguishing agent. The spent mineral oil/CDDN residue would provide significant anti-corrosion attributes, readily removable by action of water, and for most POL considerations should not be considered a "dirty" residue problem.

B. Hydrophobic fumed silica gel formulations.

Cab-o-SilTM and similar fumed silica gel formulations have the capability of absorbing significant amounts of volatile organics, including the Halons and similar halogenated extinguishing agents. On heating in a fire zone, the gelled Halon is readily liberated as the extinguishing agent. The spent silica gel would be readily removable by action of water, and for most POL considerations should not be considered a "dirty" residue problem. The silica gel would be considered as a "dirty" problem for engine fires, however. The silica gels should be efficient for lower volatility streaming agents, but probably would not be very effective for high volatility agents.

C. HypolTM, Hampshire Chem. Co. Prepolymer Gels.

Hypol agents are hydrophilic urethane which react readily with water to form gelled elastomeric products. (These materials have been used as dental foams and in other medical formulations; they are entirely non-toxic.) In the presence of volatile organics (e.g., Halons or similar volatile halogenated extinguishing agents) the gelled product is a foam containing the volatile gas.

In recent work by our group, both Halon 1211 and trifluormethyl iodide were separately trapped in sufficiently high concentrations as to readily extinguish "wastebasket" fires when the gelled Hypol formulation was scattered over the fire.

Alternatively, the gelation process could have been accomplished by introduction of the components into a fire hose and projected with a long distance stream into the fire zone. Depending on the type of Hypol agent which would be used, the gelled formulation could be thrown as a stiff foam or as an adhesive mixture which would adhere to vertical structures to liberate the Halon in a three-dimensional matrix within the fire zone.

On heating in a fire zone, the gelled Halon readily liberates the extinguishing agent. The spent Hypol residue would be removable by action of water, and for most POL considerations should not be considered a "dirty" residue problem.

SIGNIFICANCE OF RESULTS

NVP agents have greatly reduced ODP, GWP and toxic vapor properties, and pose greatly reduced atmospheric emissions due to fire extinguishing operations or from accidental releases. Agent requirements for firefighting operations would be greatly reduced, in comparison to conventional agents, most of which evaporate en route to a fire when delivered as streaming agents. Greatly extended throw ranges would result in increased safety for firefighters, since NVP agents can be projected from much greater distances. This improved agent system may be beneficial in terms of optimizing usage of Halon streaming agents in the Halon Bank.

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