A STUDY OF AIRCRAFT POST-CRASH FUEL FIRE MITIGATION

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Extensive research has been conducted on methods of controlling aircraft post-impact fuel fires. Mechanism studies of hydrocarbon fuel ignition and flame propagation have identified feasible approaches to agent selection and dispersal schemes. Selection of agents is closely controlled by guidelines of the Montreal Protocol Agreements and allowable agent manufacturing as specified by the Environmental Protection Agency. Effectiveness of agents has been determined under a variety of laboratory test conditions. Mass transport of the inerting agent into the vapor above the fuel as well as the environmental conditions in the vapor space play an important role in inerting agent effectiveness. Schemes to control hydrocarbon vapor and to enhance inerting agent effectiveness are discussed.

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EXECUTIVE SUMMARY

Problems and Objectives: The fuel fire that often follows a survivable aircraft crash continues to be a hazard. Previous research and development efforts have been unsuccessful in suppressing or preventing the fire from spilled fuel that engulfs the disabled aircraft once it has come to rest. The period immediately following the crash is the most critical time since fuel heating and ignition sources are primary factors in preventing a fire, and there is often a significant delay until ground crews gain control of the fire and perform rescue operations. Pool burning surrounding the fuselage is important not only from the standpoint of heat radiation on the surface of the fuselage but also in preventing escape or rescue of the occupants. Therefore, versatile fire-fighting agents and better methods of agent deployment are required to prevent fire on the ground surrounding the aircraft and inside the fuselage.

The goal of the present work is to conduct research that addresses the elimination of post-impact fuel fires through the use of halon-inerting agents either blended into or sprayed onto the spilled fuel.

It is the objective of this study to examine the flame-inhibiting properties of halons and determine the most effective way to use halons to prevent fuel spill fires. This study includes both an evaluation of the flame-inhibiting effectiveness of halons and an exploration of various methods of employing halons to eliminate fuel spill fires.

Importance of Project: It is well noted that halons play an important role in fire-extinguishing systems. According to the Montreal Protocol, however, in order to terminate the production of chlorofluorohydrocarbons, it will be necessary to replace the halons currently used in fire-extinguishing systems with halons that are relatively free of chlorine and bromine. Consequently, to aid in the selection of halon substitutes, it is important to investigate the fire-prevention/extinguishment mechanisms of a wide range of halons.

Technical Approach: To choose the optimal application of halons, it was necessary to measure their flame-inhibiting characteristics over a range of conditions. Although previous studies have been performed on the flame-inhibiting characteristics of halons, the one area of research that was relatively devoid of data was the condition at which the halon is dissolved in the fuel. When the halon is dissolved in the fuel, its vapors create a blanket over the fuel that is often very effective in rendering the fuel/air mixture above the liquid fuel nonflammable. In the present study, the emphasis has been to determine the effectiveness of halons as vapor-blanketing agents in fuel spill fires. Basically, three conditions were examined in this study. First, screening experiments were performed to determine the concentrations required of various halons to prevent ignition of Jet A at fuel temperatures above the flash point. This was followed by experiments to determine the effectiveness of halons in preventing ignition and flame spread over liquid pools of jet fuel. Finally, experiments were performed on the effects of halon sprays on the extinguishment of pool fires.

Accomplishments: Several halons were tested to determine their effectiveness in preventing the ignition of jet fuel spills. The measurements consisted of the closed-cup flash-point test, a pool-ignition and flame-spread test, and a spray-extinguishment test. Except for the latter, the

objective of these tests was to determine the effectiveness of halons when they are dissolved in the fuel.

It was concluded from the flash-point tests on halon-jet fuel mixtures that halon effectiveness was strongly dependent on halon composition and boiling point. Effectiveness was measured in terms of the weight percent of halon in the fuel required to prevent ignition at a temperature of about 3°C above the flash point of the fuel. A correlation of the measurements with the physical and chemical properties of the halons showed that the effectiveness was exponentially dependent on the boiling point of the halon and proportional to the total number of chemical bonds in the halon and the numbers of H, F, Cl, Br, and I atoms in the halon molecule. It was concluded from the results of the correlation that halons composed of Cl, Br, and I atoms were, respectively, 1.23, 15.19, and 21.35 times more effective than those composed of F atoms. The correlation showed that H atoms had a negative effect on the ability of the halon to prevent the ignition of jet fuel.

Experiments on open-pool ignition and flame spread showed that to prolong ignition for more than a minute, the halon concentration had to be substantially higher than that required to prevent ignition in the closed-cup flash-point test. The halons had a substantial effect on ignition lag (time required to ignite the fuel) but little or no effect on the burn time (flame propagation rate). The absolute concentration of halon in the fuel greatly influenced the effectiveness of the halon in increasing the ignition-lag time. This led to the conclusion that mass transport of halon from the liquid phase to the gas phase was very important in open-pool burning. While halons such as perfluorohexane have been found to be reasonably effective in extinguishing fires in gas phase application, it is rendered ineffective when dissolved in the fuel because its rate of mass diffusion into the vapor space above the fuel is so very slow. This mass diffusion effect is a good example of why it is very important to consider the nature of the application when halons are used in the prevention and extinguishment of fires.

All of the 21 halons examined in this study were soluble in hydrocarbons in sufficient quantities to prevent ignition of jet fuel in the closed-cup flash-point test. In fact, most of the halons examined were completely miscible in jet fuel. Perfluorohexane was the only halon found to have very limited solubility in jet fuels. Therefore, perfluorohexane is essentially ineffective in preventing pool fires because the tests indicate that it would most probably be required in concentrations above the solubility limit in this application.

Although most of the halons examined were highly soluble in jet fuel, their solutions were far from being ideal. It was concluded that Raoult's law could not be assumed in calculating the partial pressure of the halon vapor blanketing the liquid fuel.

Military Impact: It is well known that during combat, fuel tank fires and explosions are of great concern in all vehicles. Halon fire-extinguishing agents, typically Halon 1301, have been employed in military vehicles to prevent fires in the engine compartment and fuel tank areas. In view of environmental concerns over ozone depletion and global warming, halon compounds containing chlorine and bromine will be discontinued and replaced with less deleterious substitutes. The present study was made to gather data that pertains to the ultimate selection of the halon substitutes that will be used in future fire extinguishment systems for military vehicles.

FOREWORD

This work was performed by the U.S. Army Belvoir Fuels and Lubricants Research Facility (BFLRF) located at Southwest Research Institute (SwRI), San Antonio, TX, during the period July 1991 to February 1993 under Contract Nos. DAAK70-87-C-0043 and DAAK70-92-C-0059 with the Mobility Technology Center-Belvoir. Mr. T.C. Bowen (AMSTA-RBFF) of the U.S. Army TARDEC Mobility Technology Center-Belvoir served as the contracting officer's representative; Messrs. M.E. LePera (AMSTA-RBF), and E. Klueg and H.S. Byrnes (Federal Aviation Administration Technical Center) served as the project technical monitors.

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I. INTRODUCTION

The fuel fire that often follows a survivable aircraft crash continues to be a hazard. Previous research and development efforts have been unsuccessful in suppressing or preventing the fire from spilled fuel that engulfs the disabled aircraft once it has come to rest. The period immediately following the crash is the most critical time since fuel heating and ignition sources are primary factors in preventing a fire, and there is often a significant delay until ground crews gain control of the fire and perform rescue operations. Pool burning surrounding the fuselage is important not only from the standpoint of heat radiation to the surface of the fuselage but also in preventing escape or rescue of the occupants. Therefore, versatile fire-fighting agents and better methods of agent deployment are required to prevent fire on the ground surrounding the aircraft and inside the fuselage.

In view of the fact that halons have been used successfully as fire-extinguishing agents in several aircraft applications, they are being considered for preventing the fire that follows a fuel spill in a survivable aircraft crash. The goal of this project is to identify and evaluate potential extinguishing agents for the control of fuel spill fires following a survivable airplane crash.

II. BACKGROUND

The most commonly used agents to control spilled fuel burning today are Aqueous Film-Forming Foam (AFFF) or other surface active agents that lower the surface tension of hydrocarbon fuels and water. This floating film acts to reduce vaporization of the hydrocarbon fuel, thus reducing the rate of flame propagation across the fuel surface and acting as a heat sink to reduce the heat of the fuel, thus further reducing vaporization. While the film-forming foams can be very effective, they are essentially a one-dimensional agent with reduced effectiveness when the fuel surface is not flat or continues to spill from the source.

Halons are known to be extremely effective in reducing fires and flame inhibition; however, the widespread use of halons is coming under increasingly rigid controls over manufacturing and application. The future availability of fire-control halon agents is an important part of this study of potential concepts for post-impact fuel fire mitigation.

A. Agent Restrictions

Halon fire-fighting agents have a negative impact on the environment and, therefore, are being phased out by federal agencies. The stability of the halons provides for compatibility and low toxicity; their thermal and chemical activities provide efficient suppression for widely varying fire scenarios. However, their chemical components of bromine and chlorine, along with their chemical stability, allow entry into the stratosphere where photolytic and chemical activities release the halogens that catalytically destroy the Earth's protective ozone layer. The Chief of the U.S. Environmental Protection Agency (USEPA) announced in April 1991 that the Earth's ozone layer is thinning twice as fast as previously believed.

Originally, the production of the conventional halon fire-fighting agents such as 1301 would be phased out by the year 2000. More recent amendments to the Montreal Protocol call for production of Halon 1301 to stop by 1 January 1994. The protocol started with a 15-percent reduction in 1991, to be increased to 50 percent by 1995, followed by 100 percent in the year 2000; also, the new tax for Halon 1301 will be $26.50/lb in 1994. It is not anticipated that agents with the overall excellent characteristics of the existing streaming and flooding halons will be available in the near future. Instead, it is projected that multiple agents with good characteristics for particular applications will become available and that highly qualified system designs will be required to provide efficient, active fire protection. Industry has already offered some potential halon-type alternatives. Some of these replacements are being rejected due to toxicological factors, and others are failing due to the Amendments to the Clean Air Act. Potential near- and mid-term halon-type alternate agents have been identified for immediate research. Analysis and testing are necessary to evaluate their efficacy for particular applications.

The halons have so many desirable properties that they are very difficult to replace. General-purpose, direct replacements having attributes equal to those of the present halons are unlikely in the foreseeable future. However, clean alternative agents with lower ozone-depleting potential for specific uses are a realistic goal. A number of alternative agents, varying according to application, are the likely result of the search to replace the current chemicals.

B. Ozone Problem

A layer of ozone, a triatomic form of oxygen, exists in the Earth's stratosphere and acts as a barrier to harmful solar rays, filtering out a large fraction of solar UV-B radiation to keep it from reaching the Earth's surface. Short wavelength UV-B radiation causes adverse environmental impacts including increased risk of skin cancer, cataracts, material degradation, crop damage, enhanced photochemical smog, and a general imbalance of the ecosystem. The release into the Earth's atmosphere of compounds containing halogens can lead to a decrease in the stratospheric levels of ozone.(1)*

Chlorofluorocarbons (CFCs) and halon are photodissociated by vacuum UV solar radiation in the upper reaches of the stratosphere. The bromine and chlorine atoms released in the photodissociation process act as catalysts to reduce the steady-state concentration of ozone in the stratosphere.(2) This effect is measured by the ozone depletion potential (ODP), which is calculated by the use of an atmospheric model, incorporating a complete input of chemistry, solar irradiation, and transport. Ozone depletion potential is defined as the ratio of calculated ozone column change for each unit mass of gas emitted into the atmosphere relative to the calculated depletion for the reference gas CFC-11.

C. Global Warming

The United States joined 73 nations represented in Sweden on 30 August 1990 in agreeing that man's activities are causing the Earth's atmosphere to heat up. Increases in CFC and halon atmospheric trace gases can contribute to what has been called the *greenhouse warming effect* because these compounds allow the sun's energy to reach the surface of the Earth, thereby warming it, while preventing much of that energy from being reradiated to outer space.

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* Underscored numbers in parentheses refer to the list of references at the end of this report.

The contribution of a chemical to global warming is determined by using complex atmospheric modeling and specific input data for the chemical. The term Global Warming Potential (GWP) is used to directly relate the capability of a compound to absorb radiation in the "atmospheric window" extending from 7 and 13 µm where the atmosphere is relatively transparent to infrared radiation reflected from the Earth's surface. The 7- to 13-µm region of the spectrum represents heat radiation characteristic of Earth surface temperatures, e.g., 10 µm represents a temperature of about 37°C (98°F).

Most organic chemicals and halocarbons have GWPs greater than CO_2 because they are much stronger absorbers of the Earth's infrared radiation that is normally reflected into space. Molecules such as hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs), which contain hydrogen, have lower GWPs because they are readily oxidized in the troposphere by OH radicals. On the other hand, perfluorinated hydrocarbons (FCs) containing no hydrogen have relatively longer atmospheric lifetimes and, thereby, have relatively higher GWPs because they tend to build up in the atmosphere.

D. Halon

1. Montreal Protocol

For the Montreal Protocol, the U.S. Environmental Protection Agency had limited the consumption (consumption = production – export + import) of halons to the 1986 levels beginning in 1992. The stability of CFCs, so important in their use, makes them a threat to the environment. When CFCs are released at ground level, it may take seven or more years for them to diffuse upward into the stratosphere--at least 10 miles above sea level--where they reside with a half-life of about 100 years.(3)

2. Protocol Amendments

In June 1990, 93 countries were represented in London to amend the Montreal Protocol. Agreement was reached to phase out halons and restrict other ozone depleters. Environmentalists argued that they could depend on industry to stop production of CFCs and instead make HCFC substitutes that could become popular worldwide. HCFCs are only partially halogenated, so they have relatively low ODPs because of their short lifetime in the atmosphere. However, bromine-containing halons have ODPs that are considerably greater than those of CFCs. Chlorine is the leading cause of the current rate of ozone depletion, but with significant growth, bromine could also become a major factor.

A summary of the relevant London Amendments are:

- Chlorofluorocarbon: 20-percent reduction by 1993; 50-percent reduction by 1995; 85-percent reduction by 1997; 100-percent reduction by 2000. Determine by 1992 if earlier phaseout is possible.

- Halons: 50-percent reduction by 1995; 100-percent reduction by 2000 with exemption for essential uses.

- Other fully halogenated CFCs: 20-percent reduction by 1993; 85-percent reduction by 1997; 100-percent reduction by 2000.

- HCFCs (transitional substances): resolution calling for use only when other alternatives are not feasible, with phaseout by 2020 if feasible, and no later than 2040.

3. Laws Controlling Chemicals

The recent federal documents for protecting the ozone layer are the Montreal Protocol on Substances that Deplete the Ozone Layer, which entered into effect on 1 January 1989, and the USEPA Final Rule. The Clean Air Act, published 3 August 1990, calls for a reduced consumption of halons starting at 15-percent reduction in 1991, with the same 50- and 100-percent reductions in 1995 and 2000, respectively, as the Montreal Protocol. There are exceptions for aircraft safety. The Omnibus Budget Reconciliation Act of 1989 calls for new taxes on halons. From 1990 to 1993, the tax was $0.25/lb; in 1994, the tax will be $8.00/lb for

Halon 1211 and $26.50/lb for Halon 1301; and from 1995 and beyond, it will add $1.35/lb to Halon 1211 and $4.50/lb to Halon 1301 until phaseout. Department of Defense (DOD) Directive 6050.9 directs DOD components to eliminate the unnecessary release of halon to the atmosphere, to conduct research and development on replacement agents, and to adopt suitable substitutes when consistent with mission requirements. Additional regulations restricting CFCs/halons include the Defense Authorization Act for FY 90/91, Section 356; U.S. Air Force (USAF) Regulation 19-15 (Draft); and Army (HQDA) Policy Letter 200-90-1 dated 27 July 1990, which has established a policy that all nonmission critical uses of halons will be phased out on or before October 2000.

E. Halon Replacement Technology

1. Halons

Halons are fully halogenated species and possess unusual chemical stability. The highly reactive hydroxyl radical, OH, is often responsible for chemical attack on molecules in the atmosphere and living organisms. Hydroxyl radicals are by far the most important species responsible for chemical attack in the troposphere. The strengths of the carbon-halogen bonds in halons are high compared to the relatively low-bond energies of possible products formed by the reactions with OH radicals.(4) The inertness and low polarity (nonconducting) of halons imply that they are, for the most part, nontoxic, so they are relatively noninteractive with materials in the tropospheric environment (i.e., they have good compatibility properties). However, in a flame environment, halons undergo thermal decomposition, so they are almost as reactive as hydrocarbon fuel molecules toward O/H atoms and OH radicals. The reaction products produced in combustion gases containing halons can be very corrosive and toxic.

2. HCFCs and HFCs

Compared to the halons, HCFCs and HFCs have hydrogen atoms added to the molecules, thus allowing increased chemical attack by OH in the troposphere. This increased attack results in the destruction of HCFCs and HFCs in a time frame that is short relative to their tropospheric residence time. The halon-free radicals produced by the hydrogen atom abstraction react rapidly with O_2 to form products that are supposedly soluble in water and become rained out of the atmosphere.

While the presence of hydrogen in the halon molecule is desirable from an environmental standpoint, it increases the solubility of the halon in the blood, thus increasing the potential for toxicity.

Halon alternatives have been announced by companies in America and Europe. However, most of these alternatives involve HCFCs and HFCs, and the continued use of HCFCs will be restricted by the Montreal Protocol Amendments. The likelihood of commercial offerings of halon alternatives other than those already announced is indicated by the fact that, although the selected HCFCs did allow rapid entry into the marketplace, all the primary commercial halon manufacturers have large research and development programs. It is important to realize that the production and availability of halon alternatives will be a function of the user requirements.

3. Low ODP Agents

Compounds that do not contain chlorine and bromine atoms have low ODPs. Fire-fighting agents consisting of perfluorinated organics are being considered because fluorine has no significant effect on stratospheric ozone.

Another approach for low ODP fire-fighting agents is to use compounds that are readily destroyed in the troposphere. It is possible to create species that will react in sunlight. This reaction can be done by extending the absorption region of a compound toward the red so that the compound will react photochemically and become oxidized in the troposphere, allowing its reaction products to be rained out. In this respect, iodine compounds are of interest because they are photosensitive and make effective fire-fighting agents.

F. Potential Halon Alternatives

TABLE 1 lists some potential halon-type alternate agents taken from recent studies to optimize agent selection. There is a wide span in the characteristics of the selected candidates that warrant analyses. Testing needs to be done to evaluate how the property characteristics affect application. The variations in the recommended agents' properties are: (a) more than 100°C in boiling point; (b) almost a factor of 3 in ΔH, k; (c) a factor of over 50 in vapor pressure; (d) a factor of 2 in C_ps; (e) a factor of over 25 for thermal conductivity; (f) a factor of almost 700 in cost, k; (g) unknown toxicity factors; and (h) factors of over 2 in weight volume effectiveness. Engineering research and development should be accomplished for optimization toward applications.

G. Commercial Alternatives

The current commercial offerings of alternative fire-fighting agents consist mostly of HCFCs and HFCs. These are considered to be the near-term agents for replacing the current halon production since the major manufacturers (a) have been seeking replacements for the past few years; (b) have practically optimized the producibility, compatibility, toxicity, and capability of these agents; and (c) have spent the most funds to provide alternatives. The U.S. Air Force has developed a data base to aid in the selection of streaming agents to be tested. The most recent agents identified (5) as potential streaming agents are HCFC-123, offered by DuPont as FE-232, and PFH (perfluorohexane).

III. OBJECTIVE

The goal of this project is to conduct research that addresses the elimination of post-impact fuel fires through the use of inerting agents either blended into or sprayed onto the spilled fuel.

It is the objective of this study to examine the flame-inhibiting properties of halons and to determine the most effective method of using halons to prevent fuel spill fires. This includes both the determination of which halons are the most effective flame inhibitors and an exploration of various methods of employing halons to eliminate fuel spill fires.

While fire prevention is paramount in this study, the selection of halons and their method of application will be greatly influenced by economic and environmental concerns. Therefore, an important element in this program will be to coordinate this research with changes in agent development and availability as mandated by government regulations.

IV. APPROACH

To choose the optimal application of halons, it is necessary to measure the flame-inhibiting characteristics of halons under several conditions. Although previous studies have been performed on the flame-inhibiting characteristics of halons, the one area of research relatively devoid of data is the condition in which the halon is dissolved in the fuel. When the halon is dissolved in the fuel, its vapors create a blanket over the fuel that is often very effective in rendering the fuel/air mixture above the liquid fuel nonflammable. The emphasis in the present study is to determine the effectiveness of halons as vapor-blanketing agents in fuel spill fires. Basically, three conditions have been examined in this study. First, screening experiments were performed to determine the concentrations required for various halons to prevent ignition of Jet A at fuel temperatures above the flash point. These experiments were followed by tests to determine the effectiveness of halons in preventing ignition and flame spread over liquid pools of jet fuel. Finally, experiments were performed on the effects of halon sprays on the extinguishment of pool fires.

V. RESULTS AND DISCUSSION

A. Flash-Point Measurements

The Pensky-Martin and Seta-flash closed-cup flash-point testers were used to determine the efficacy of halons in inhibiting ignition of the vapors of Jet A fuel. Most of these measurements were performed with the Seta-flash tester because it required a relatively small sample size (2 mL) and could be used to measure flash point at a set temperature. The smaller sample size requirement was especially helpful in situations where the toxicity of the halon was high and when the halon was in short supply.

The experimental procedure begins with dissolving a measured amount of halon in the Jet A fuel and determining if there is a flash point. The Jet A fuel selected for the measurements has a flash point of 54°C in the Pensky-Martin and Seta-flash closed-cup testers. The flash point and fire point measured with the Cleveland open-cup tester were both 74°C. While testing the halon/fuel mixtures in the Seta-flash closed-cup tester, the observations of flash point were made at a fuel temperature of 57°C. If the mixture flashes, the procedure is repeated using a higher concentration of halon until the mixture is unable to ignite. TABLE 1 gives the results of the flash-point measurements on all the halons examined except trifluoroiodomethane. The table lists the boiling point, the concentration of halon in the liquid fuel required to prevent flash, the calculated volume percent of halon in the vapor phase, and a halon effectiveness parameter, ϵ, defined later in this section.

The flash-point measurements on trifluoroiodomethane were performed with n-decane instead of Jet A because the vapor pressure of the agent was too high. Mixtures of trifluoroiodomethane and decane were prepared by dispersing the gaseous agent through decane. A large portion of the gas dissolved in the decane, but some escaped to the atmosphere. If the base fuel had been Jet A, the escaped halon gas would have carried away the light ends of the fuel and changed the fuel's flash point. The flash point of a pure substance such as decane is not affected by evaporation.

TABLE 1. Flame Inhibition Efficacy of Halons Determined by Flash-Point Test

Halon Description	Halon Boiling Point,°C	No Flash Halon Conc., wt%	Vol% Halon in Vapor Space, Calc.*	Efficacy (e) Relative to CH_2ClBr
Bromochloro Methane (CH_2ClBr)	68.0	2.13	2.0	1.00
Carbon Tetrachloride (CCl_4)	78.6	10.39	6.0	0.25
Methylene Chloride (CH_2Cl_2)	40.5	6.25	20.3	0.22
Methylenebromide (CH_2Br_2)	98.2	2.29	0.6	1.25
1,1,2-Trichloro-1,2,2-Trifluoroethane ($ClCF_2CFCl_2$)	47.5	3.39	4.2	0.91
Ethyl Bromide (C_2H_5Br)	38.4	2.21	6.3	0.81
Trichloro-Ethylene ($ClCH{=}CCl_2$)	85.7	36.25	16.7	0.06
Chloroform ($CHCl_3$)	61.3	8.13	9.8	0.24
Bromochlorotrifluoro Ethane ($CHClBrCF_3$)	50.2	1.15	1.3	2.83
Dichlorotrifluoro Ethane ($CHCl_2CF_3$)	24.0	2.00	5.6	1.26
Ethyl Iodide (C_2H_5I)	71.2	6.90	4.8	0.37
Methyl Iodide (CH_3I)	42.5	1.00	1.9	2.34
Methylene Iodide (CH_2I_2)	181.0	13.83	0.2	0.32
Difluorotetrachloro Ethane ($C_2F_2Cl_4$)	91.0	8.03	2.3	0.42
Difluorodibromo Methane (CF_2Br_2)	22.5	0.38	0.9	9.14
Dichlorobromo Methane ($CHCl_2Br$)	87.0	2.55	0.8	1.35
Trichloro Fluoromethane ($CFCl_3$)	23.7	1.71	6.2	1.33
Dibromofluorochloro Methane ($CFClBr_2$)	79.5	1.79	0.7	1.57
Dibromotetra-Fluoroethane ($C_2F_4Br_2$)	47.0	0.61	0.6	7.00
Perfluorohexane (C_6F_{14})	56.0	0.90	0.5	6.21

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* Calculated assuming the halon/fuel mixture is an ideal solution.

Twenty-one halons ranging widely in boiling point and composition were examined. The objective was to determine the effectiveness of the halons in preventing ignition (flash) of the fuel vapors. Two definitions of halon effectiveness are given in TABLE 1. The first definition (column 4, TABLE 1) is based on the understanding that halons prevent fire by a vapor-blanketing mechanism.(6) In that case, effectiveness is defined as the volume percent of halon vapor required in the vapor space to prevent ignition of Jet A. The lower the volume percent halon required to prevent ignition, the greater the effectiveness.

In the second definition (column 5, TABLE 1), the effectiveness, ε, is expressed as

$$\varepsilon = \frac{M_w}{100w} \qquad \text{(Eq. 1)}$$

where M_w is the molecular weight and w is the weight percent halon dissolved in the fuel. Equation 1 conveys that ϵ is inversely proportional to the molar concentration of halon in the fuel.

Both definitions of halon effectiveness are relevant. The volume percent of halon required in the vapor space is of interest because it can be compared with previously measured volume percents of halon vapors required to prevent ignition of premixed gas-phase fuel/air mixtures.(7) The definition expressed by Equation 1 is more practical because it is a direct measure of the effectiveness of halons dissolved in Jet A fuel.

The volume percent halon given in column 4 of TABLE 1 to prevent ignition is the concentration in the vapor space calculated at 57.2°C (i.e., 3°C above the flash point of Jet A). The volume percent of halon in the vapor space is expressed as

$$C_H = 100\frac{P_v}{P_t} \qquad \text{(Eq. 2)}$$

where P_t is the total pressure, and P_v is the partial pressure of halon vapor above the fuel expressed as

$$P_v = X_{Halon} P_{Halon} \qquad \text{(Eq. 3)}$$

where X_{Halon} is the mole fraction of halon in the Jet A fuel, and P_{Halon} is the vapor pressure of the pure halon calculated via the Clapeyron-Clausius equation.(8) Equation 3 is an expression of Raoult's Law (8), which assumes that the halon/fuel mixture is an ideal solution. At first glance, this assumption appeared to be reasonable for most of the halons except for perfluorohexane, which had only limited solubility in jet fuel. To calculate P_{Halon}, the heat of vaporization, ΔH_{vap}, of the halon is required. Because several of the heats of vaporization were not known, a correlation of ΔH_{vap} with the boiling point T_{bp} of the halon was developed from the data that were available. Fig. 1 shows a linear correlation of the known heats of vaporization, ΔH_{vap}, with boiling points, T_{bp}, of the halons. The correlating equation expressed as

$$\Delta H = 23.21 T_{bp} - 611.7 \qquad \text{(Eq. 4)}$$

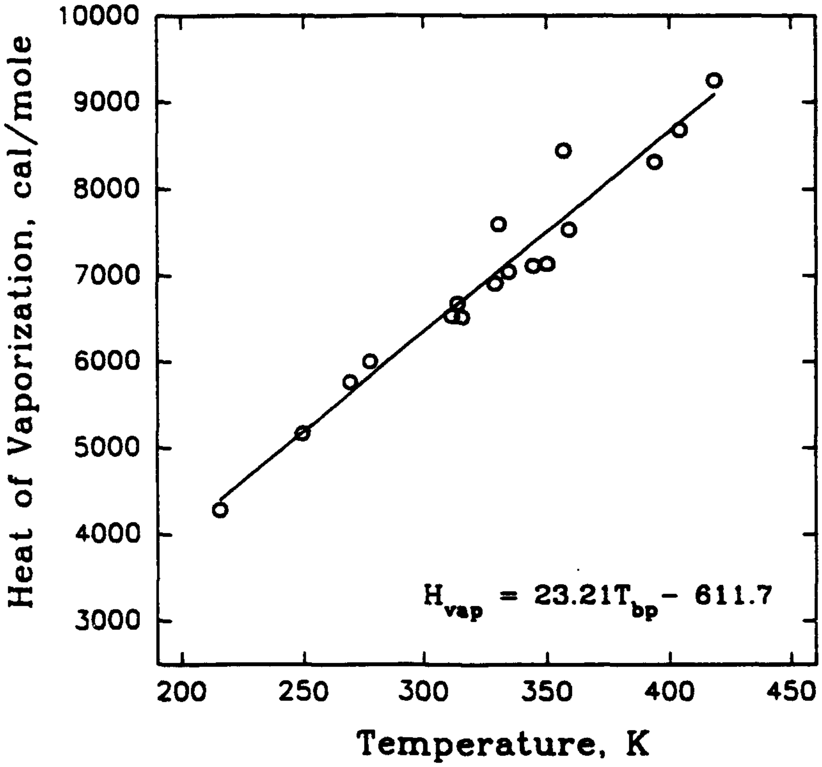

Figure 1. Correlation of the heats of vaporization of halons with their boiling point temperature

was used in the Clapeyron-Clausius equation to calculate P_{Halon}. Column 4 of TABLE 1 gives the results of the calculations in terms of volume percent of halon in the vapor space above the fuel.

Fig. 2 compares the halon vapor concentrations listed in TABLE 1 with the halon vapor concentrations required to suppress ignition of premixed fuel/air mixtures.(7) The flammability limit data (7) were obtained by determining the minimum volume percent of halon vapor required to prevent ignition of a heptane/air mixture. These measurements were performed over a range of equivalence ratios to determine the optimum condition for ignition and flame propagation.

The results in Fig. 2 show a significant disparity between the volume percents calculated from the flash-point measurements and those obtained from the flammability limit measurements. In general, the calculated volume percents are substantially lower than the corresponding values obtained from the flammability measurements. Only the calculated values for ethyl bromide and ethyl iodide compare favorably with the flammability limit data. It is concluded from the results

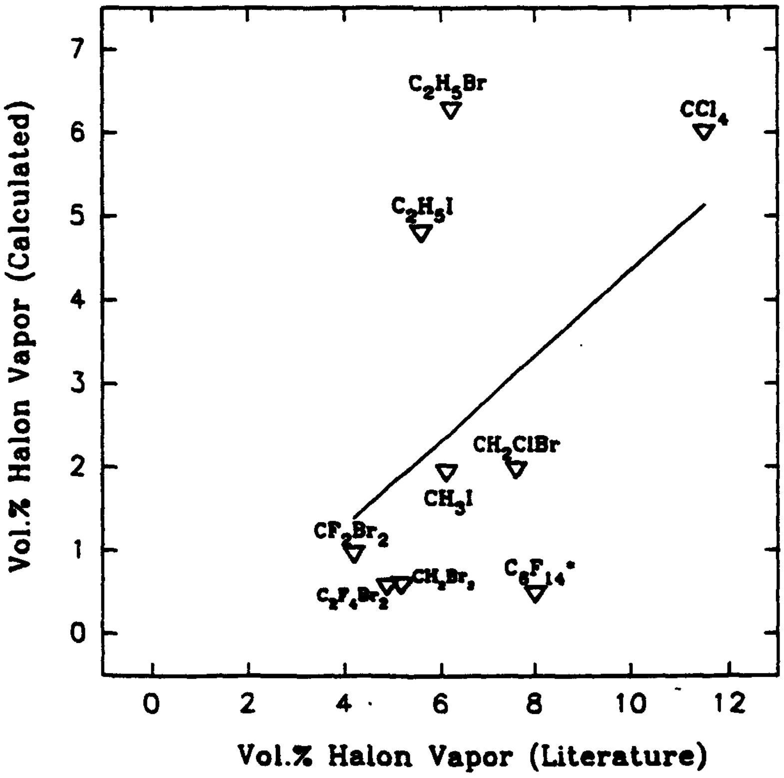

Figure 2. Comparison of halon vapor concentrations calculated assuming Raoult's law with values from the literature determined in flammability limit studies

in Fig. 2 that the halon/Jet A fuel mixtures are nonideal solutions. In other words, the halon real vapor pressures are substantially higher than the values calculated assuming Raoult's law.

Fig. 3 shows an example of where the departure from Raoult's law is relatively strong. The figure shows Clapeyron-Clausius plots of Reid vapor pressure of pure perfluorohexane and a perfluorohexane/Jet A blend. Perfluorohexane was of particular interest in this study because it has a zero ODP and is considered by the fire research community to be an effective fire-extinguishing agent. The Reid vapor pressure measurements were made with a Grabner model CCA-VPS Vapor Pressure Tester. For pure perfluorohexane, the heat of vaporization is 6907 cal/mole, while the perfluorohexane/Jet A solution gives a value of 2276 cal/mole. Note that only the vapor pressure of perfluorohexane is plotted in Fig. 3; the partial vapor pressure contributed by the Jet A fuel was negligible. The apparent heat of vaporization obtained from the perfluorohexane solution data is much lower than that of the pure perfluorohexane because the vapor pressure deviates strongly from that calculated using Raoult's law. The deviation from Raoult's law stands to reason because perfluorohexane has only limited solubility in Jet A fuel.

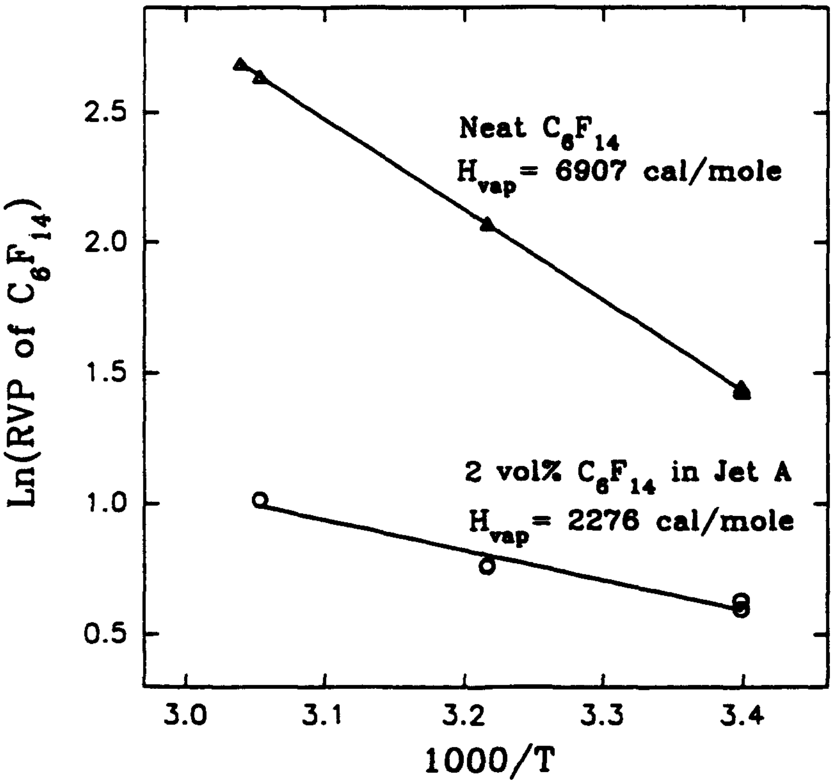

Figure 3. A Clapeyron-Clausius plot of the vapor pressure of pure perfluorohexane and a 2 vol% solution of perfluorohexane in Jet A

Fig. 4 shows the solubility of perfluorohexane in Jet A over a range of temperatures. Most of the halons examined in this study were miscible in Jet A in all proportions. The exception, perfluorohexane, is not just sparingly soluble; it is very slow to dissolve in Jet A because of its low solubility. This low solubility could present a problem in the use of perfluorohexane as a fire-extinguishing agent. For example, if droplets of perfluorohexane were to be sprayed onto jet fuel, they would probably sink to the bottom rather than dissolve at the surface where they would be most effective in vapor-blanketing a fuel spill.

Fig. 5 compares the Clapeyron-Clausius plots of the measured and calculated vapor pressures of the perfluorohexane/Jet A solution. The figure shows a substantial departure of the measured vapor pressure from that calculated using Raoult's law. The measured volume percent of perfluorohexane vapor turns out to be about an order of magnitude greater than the calculated value. Interestingly, the volume percent determined from vapor pressure measurements compares favorably with the value of ≈8 vol% estimated from flammability limit data.(7) Also, note this result in Fig. 2.

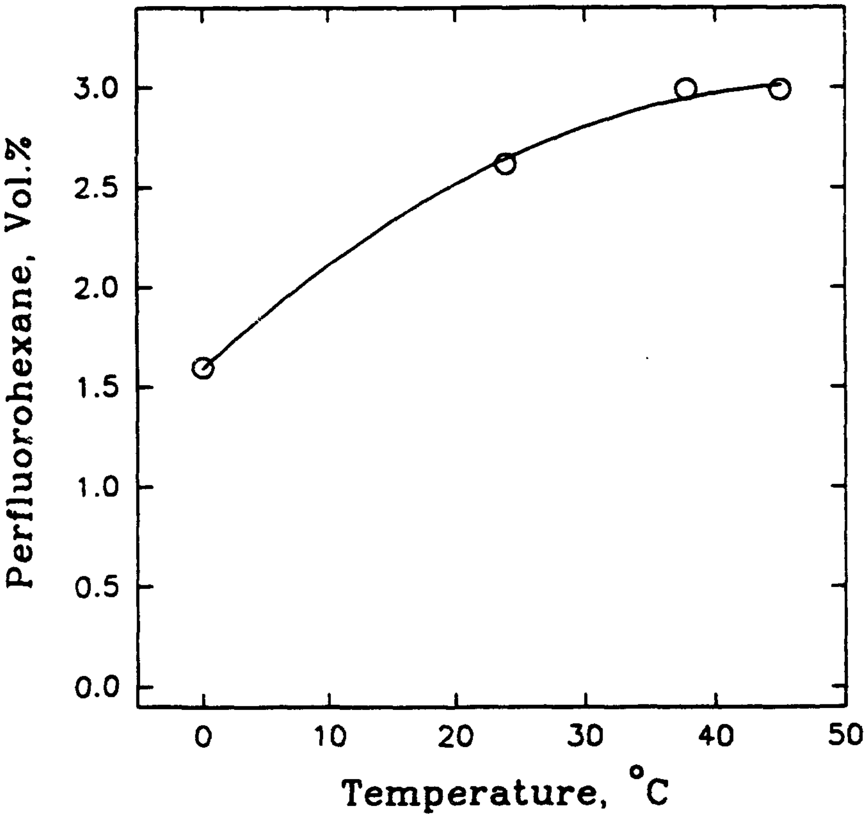

Figure 4. Effect of temperature on solubility of perfluorohexane in Jet A

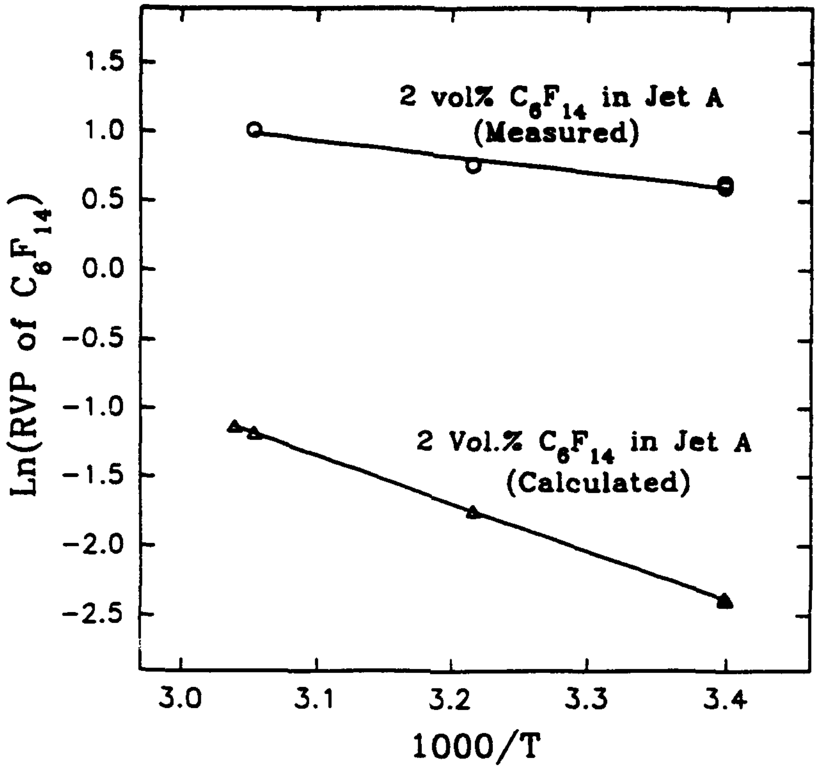

Figure 5. Comparison of measured vapor pressures with calculated vapor pressures of a 2 vol% solution of perfluorohexane in Jet A

Since it is not cogent to assume that mixtures of halons in jet fuel are ideal solutions, the calculated volume percent of halon required to prevent ignition in the flash-point tester must only be considered a qualitative measure of halon effectiveness. The parameter, ε, expressed in Equation 1, is a more appropriate measure of halon effectiveness. A nonlinear regression analysis was used to correlate ε with the halon composition and boiling point. The results of the correlation shown in Fig. 6 are expressed as

$$\varepsilon = 1.38 \times 10^{-6} B \left(N_F + 1.23N_{Cl} + 15.19N_{Br} + 21.35N_I - 2.42N_H\right)\exp(3199.3/T) \qquad \text{(Eq. 5)}$$

where B is the total number of chemical bonds, T is the absolute temperature in °K, and N_H, N_F, N_{Cl}, N_{Br}, and N_I are the numbers of H, F, Cl, Br, and I atoms in the halon molecule. It is clear from the plot of predicted versus measured ε's in Fig. 6 that Equation 5 gives an accurate prediction of the halon effectiveness values recorded in TABLE 1.

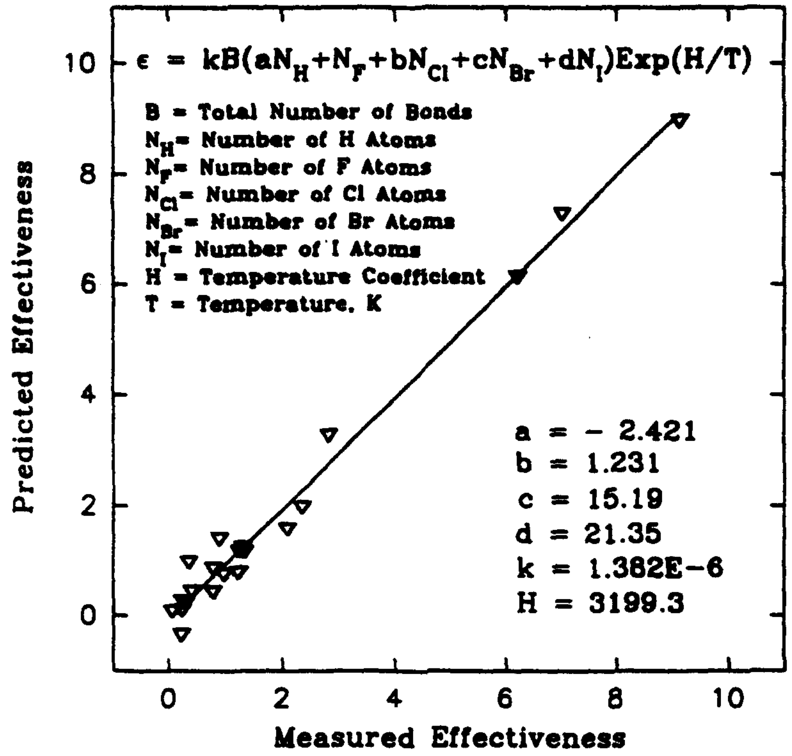

Figure 6. <u>A comparison of the halon effectiveness, ε, with the measured values in TABLE 1</u>

(The values of ε are normalized such that ε for bromochloromethane is unity.)

The correlation in Fig. 6 shows that halon effectiveness, ε, is directly proportional to the number of chemical bonds and depends strongly on the chemical composition and boiling point. The correlation indicates that ε depends on both physical and chemical properties of the halon. The dependence on the number of chemical bonds is related to the heat capacity of the halon. The higher the heat capacity, the greater the heat sink capability of the halon. The relative efficiency of the atom types in the molecule seems to be related to the chemical mechanism of flame inhibition. The coefficients of the terms N_{Cl}, N_{Br}, N_I, and N_H in the correlation are normalized with respect to the N_F term so they define the relative fire-extinguishing potencies of each atom type. The results show that halons that contain bromine and iodine are more than an order of magnitude more effective than those that contain fluorine and chlorine. This difference suggests that halons containing bromine and iodine inhibit ignition by a chemical mechanism. Since fluorocarbons are very stable and unreactive, their effects are mostly physical. Iodine seems to be more effective than bromine on a molar basis while bromine is most effective on a weight basis.

From the standpoint of the ozone depletion potential, iodine may be the most favored halon constituent. Halons containing chlorine and bromine are relatively stable and resistant to solar photolysis, while the halons containing iodine tend to photolyze quickly in the troposphere. As a result, they have little or no chance of reaching the ozone layer. These conclusions are in good agreement with those of Sheinson, et al.(9)

1. Fuel Volatility

It was also important in this study to determine if the effectiveness of halons is significantly influenced by the flash point of the test fuel. Ignition tests in the Seta-flash closed-cup flash-point tester were performed to determine halon effectiveness in a relatively low flash-point (100°F) JP-4/Jet A blend. The JP-4/Jet A blend was prepared by adding approximately 10 wt% of a debutanized JP-4 to Jet A. Measurements of the weight percent of dissolved halon required to prevent ignition of the JP-4/Jet A test fuel were performed on six halons. To be consistent with previous tests performed with neat Jet A, the flash-point measurements were made 5 degrees above the flash point of the JP-4/Jet A blend, i.e., 105°F. Recall that the closed-cup flash point of the neat Jet A was 129°F, and the tests were conducted at 135°F. TABLE 2 shows the results of these tests and compares them with the weight percents of halon required to prevent ignition of neat Jet A.

The results in TABLE 2 are somewhat ambiguous in that in some instances, the weight percent halon required to prevent ignition of the JP-4/Jet A blend was greater than that for neat Jet A, while in other cases it was lower. It was expected that a higher weight percent of halon would be required to prevent ignition of the lower flash-point fuel because the vapor pressure of the halon is less at 105°F than it would be at 135°F. It is not clear why most of the halon weight percents are lower for the 105°F flash-point fuel. The ignition chemistries of the JP-4/Jet A blend and the neat Jet A are expected to be the same, so the halons should have the same flame-inhibiting effect on each fuel.

TABLE 2. The Effect of Base-Fuel Flash Point on Weight Percent Halon Required to Prevent Ignition

Halon	Halon, wt%, 38°C (100°F) Flash Point	Halon, wt%, 54°C (129°F) Flash Point
Difluorodibromo Methane (CF_2Br_2)	0.29	0.38
Carbon Tetrachloride (CCl_4)	4.30	10.40
Methylene Chloride (CH_2Cl_2)	7.10	6.30
Bromochloro Methane (CH_2ClBr)	1.10	2.10
Trifluorotrichloro Methane ($C_2F_3Cl_3$)	2.40	3.40
Trifluorodichloro Methane ($C_2HF_3Cl_2$)	3.00	2.00
Perfluorohexane (C_6F_{14})	0.94	0.90

2. Agent Volatility

The flash-point measurements were performed using n-decane and dodecane as fuels because there was a concern that the light ends of a multicomponent fuel could be displaced by the CF_3I gas as it was dissolved into the fuel. Trifluoroiodomethane (CF_3I) is a relatively dense gas that boils at about −21°C. It was dissolved into the fuel by passing the gas through a dispersion tube into the fuel. It appeared to be reasonably soluble in the fuel, but if left to stand, it would evaporate from the fuel in a matter of minutes. Fig. 7 shows how fast CF_3I evaporates out of decane at room temperature. The CF_3I/decane solution was added to a depth of about 5 mm in a 50-mL beaker, and its weight loss was monitored continuously. The evaporation rate of the CF_3I was quite fast at first, but then reached a relatively constant rate after the concentration dropped below 0.4 wt%.

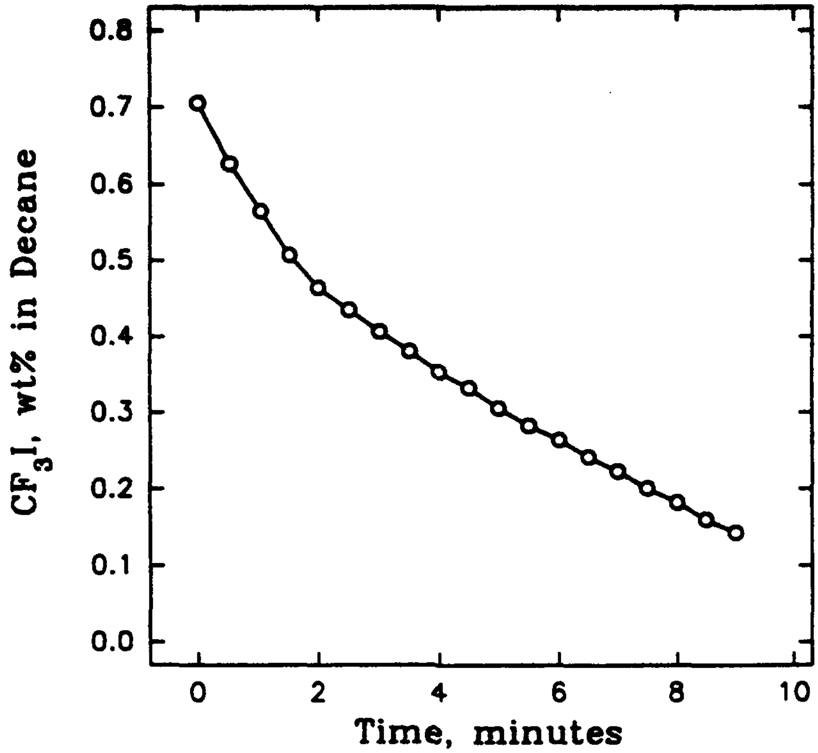

Figure 7. The evaporation of CF_3I from a semisaturated solution of CF_3I in n-decane at room temperature

The flash-point measurements were made at 120° and 165°F, which were approximately 5°F above the flash points of n-decane and n-dodecane, respectively. The weight percent concentrations of CF_3I required to prevent ignition were 0.465 for n-decane and 0.333 for n-dodecane. These results support the idea that the concentration of halon required to prevent ignition should decrease as the flash point of the fuel is increased.

B. Flame-Spreading Experiments

The objective of the flame-spreading experiments was to determine the effectiveness of halons in preventing flame spread from an ignition source isolated from the fuel treated with halon. These measurements were performed in a heated flame trough of approximately 90 cm in length, 8 cm in width, and 1 cm in depth (30 × 3 × 0.4 in.). In the test procedure, the flame trough was filled with 460 mL of fuel preheated to 57°C, or about 3°C above the closed-cup flash point of Jet A. A wick located at one end of the trough was saturated with neat fuel and ignited. The wick flame, which was in intimate contact with halon/Jet A mixture in the trough, served as the ignition source. Once the halon/Jet A mixture ignited, the flame would spread at a relatively uniform rate over the length of the trough. Two parameters, ignition lag and burn time, are measured. The ignition lag is the time required for the wick flame to ignite the fuel, and the burn time is the duration of flame travel over a distance of 61 cm in the trough. The ignition lag was the most important parameter because it was a measure of how long the halon would prevent the flame from spreading.

TABLE 3 shows the ignition lag and burn time test results on several halons using Jet A as the base fuel. TABLE 4 shows similar results for the lower flash-point JP-4/Jet A blend. Note that the first row of data in TABLES 3 and 4 gives the average ignition lag and burn time results, respectively, for the neat jet fuels. The remaining rows in the tables show ignition lags and burn times for increasing weight percent halon beginning with the weight percent halon required to prevent ignition of the fuel in the closed-cup flash-point tests (see TABLE 1).

After the flame-spreading tests on the halons included in TABLES 3 and 4 were completed, it became evident that similar tests should have been performed to determine the effectiveness of perfluorohexane in preventing flame spread. The tests were performed in a heated flame trough on both Jet A and the lower flash-point JP-4/Jet A blend using four concentrations of perfluorohexane in each of the test fuels. TABLES 5 and 6 give the respective measurements of ignition lag and burn time.

TABLE 3. Flame Spread Over Jet A Fuel at 57°C (135°F) in the Flame-Spreading Trough

[Ignition lag and burn time were measured at halon concentrations starting
with the weight percent halon required to prevent ignition in the
closed-cup Seta-flash tester (see TABLE 1)]

Halon	Halon, wt%	Ignition Lag, s	Burn Time, s	Halon, wt%	Ignition Lag, s	Burn Time, s
Neat Jet A	0.00	12.8 ± 3	11.2 ± 1.5	0.00	12.8 ± 3	11.2 ± 1.5
Dibromodifluoro Methane (CF_2Br_2)	0.38	NM*	NM	0.47	NM	NM
Dichlorobromo Methane ($CHCl_2Br$)	2.55	18.1	19.1	3.19	22.6	20.5
Chloroform ($CHCl_3$)	8.13	NM	NM	10.16	NM	NM
Trichlorofluoro Methane ($CFCl_3$)	1.71	14.7	14.3	2.14	16.8	13.2
Dibromochloro Fluoromethane ($CFClBr_2$)	1.79	22.9	19.2	2.24	25.0	18.6
Carbon Tetrachloride (CCl_4)	10.39	96.0	19.7	12.99	>240	NM
Methylene Chloride (CH_2Cl_2)	6.35	12.9	14.8	7.81	NM	NM
Bromochloro Methane (CH_2ClBr)	2.13	19.4	16.8	2.66	24.3	19.9
Methyl Iodide (CH_3I)	1.00	12.3	17.2	1.25	13.1	16.7
Trifluorobromo Chloroethane (C_2HF_3ClBr)	1.15	NM	NM	1.44	16.2	15.4
Trifluoro Trichloro Ethane ($C_2F_3Cl_3$)	3.39	13.3	15.7	4.24	16.8	15.2
Tetrafluoro Dibromo Ethane ($C_2F_4Br_2$)	0.61	20.0	13.7	0.77	16.8	17.4
Ethyl Iodide (C_2H_5I)	6.98	29.1	23.6	8.73	66.1	11.2
Dichloro Trifluoroethane ($C_2HF_3Cl_2$)	2.00	11.2	14.0	2.50	9.6	14.6
Tetrachloro Difluoro Ethane ($C_2F_2Cl_4$)	8.03	NM	NM	10.04	NM	NM
Neat Jet A	0.00	12.8 ± 3	11.2 ± 1.5	0.00	12.8 ± 3	11.2 ± 1.5
Dibromodifluoro Methane (CF_2Br_2)	0.76	17.1	15.5	0.95	35.2	15.2
Dichlorobromo Methane ($CHCl_2Br$)	5.10	65.5	29.2	6.38	71.1	35.1
Chloroform ($CHCl_3$)	16.25	>240	NFS	20.31	NM	NM
Trichlorofluoro Methane ($CFCl_3$)	3.42	NM	NM	4.28	45.7	15.2
Dibromochloro Fluoromethane ($CFClBr_2$)	3.58	35.4	18.0	4.48	42.0	28.7
Carbon Tetrachloride (CCl_4)	20.78	>240	NFS	25.98	NM	NM
Methylene Chloride (CH_2Cl_2)	12.50	24.8	44.6	15.63	109.6	25.8
Bromochloro Methane (CH_2ClBr)	4.26	37.8	35.0	5.33	206.9	31.0
Methyl Iodide (CH_3I)	2.00	25.5	18.0	2.50	27.8	18.7
Trifluorobromo Chloroethane (C_2HF_3ClBr)	2.30	32.5	16.8	2.88	46.9	16.8
Trifluoro Trichloro Ethane ($C_2F_3Cl_3$)	6.78	99.2	13.3	8.48	261.8	12.7
Tetrafluoro Dibromo Ethane ($C_2F_4Br_2$)	1.22	17.4	16.8	1.53	23.6	17.4
Ethyl Iodide (C_2H_5I)	13.97	NM	NM	17.46	>240	NFS
Dichloro Trifluoroethane ($C_2HF_3Cl_2$)	4.00	14.3	15.9	5.00	40.7	18.9
Tetrachloro Difluoro Ethane ($C_2F_2Cl_4$)	16.06	112.5	22.9	20.08	NM	NM

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* NM = No Measurement.
NFS = No Flame Spread.

TABLE 4. Flame Spread Over a JP-4/Jet A Blend at 41°C (105°F)

[Induction period and burn time were measured in a shallow 90- × 8- × 1-cm (30- × 3- × 0.4-in.)] trough. The closed-cup flash point of the JP-4/Jet A blend was 38°C (100°F)]

Halon	Halon, wt%	Ignition Lag, s	Burn Time, s	Halon, wt%	Ignition Lag, s	Burn Time, s
None	0.00	25.0	15.9	0.000	25.0	15.9
CF_2Br_2	0.29	35.1	19.7	0.577	30.2	18.9
CCl_4	4.27	29.4	18.1	8.552	51.0	NM*
CH_2Cl_2	7.05	11.9	27.9	14.100	158.2	41.4
CH_2ClBr	1.14	31.7	21.3	2.280	67.7	19.2
$C_2F_3Cl_3$	2.36	25.4	15.7	4.720	36.9	19.3
$C_2HF_3Cl_2$	2.99	14.0	17.7	5.980	127.4	17.8

* NM = Not Measured.

TABLE 5. Ignition-Lag Times Over Jet A at 57°C (135°F) and JP-4/Jet A Blend at 41°C (105°F)

[Flame spread measured in a 90- × 8- × 1-cm (30- × 3- × 0.4-in.) trough]

Halon/Fuel Mix	Halon, wt%	Ignition Lag, s	Halon, wt%	Ignition Lag, s	Halon, wt%	Ignition Lag, s	Halon, wt%	Ignition Lag, s
Jet A	0.00	26.0	0.00	26.0	0.00	26.0	0.00	26.0
C_6F_{14} Jet A	0.90	31.8	1.35	28.8	1.8	25.1	2.25	31.6
JP-4/Jet A	0.00	25.0	0.00	25.0	0.00	25.0	0.00	25.0
C_6F_{14} JP-4/Jet A	0.94	27.4	1.41	27.4	1.88	24.6	2.35	23.3

TABLE 6. Burn Times Over Jet A at 57°C (135°F) and JP-4/Jet A Blend at 41°C (105°F)

[Flame spread measured in a 90- × 8- × 1-cm (30- × 3- × 0.4-in.) trough]

Halon/Fuel Mix	Halon, wt%	Burn Time, s	Halon, wt%	Burn Time, s	Halon, wt%	Burn Time, s	Halon, wt%	Burn Time, s
Jet A	0.00	14.5	0.00	14.5	0.00	14.5	0.00	14.5
C_6F_{14} Jet A	0.90	13.2	1.35	12.9	1.80	12.8	2.25	13.8
JP-4/Jet A	0.00	15.9	0.00	15.9	0.00	15.9	0.00	15.9
C_6F_{14} JP-4/Jet A	0.94	16.2	1.41	14.9	1.88	16.3	2.35	15.5

It is important to note that when the second series of experiments was conducted, the laboratory ambient temperature was about 10°F lower than when the initial flame-spreading tests were performed on the halon/JP-4/Jet A blends (see TABLE 4) and perfluorohexane. As a result, the ignition lags measured for the neat Jet A and JP-4/Jet A blend were about 26 seconds instead of the usual 12.8 seconds. In comparing the results of perfluorohexane with those of the other halons in TABLE 3, the ignition lags given in TABLE 5 were therefore normalized relative to the 12.8-second time.

An inspection of the results given in TABLES 3 and 4 show that the halon weight percent required to prevent flame spread is much higher than the weight percent needed to prevent ignition in the closed-cup flash-point test. While most of the halons caused an increase in the ignition lag, the burn times of the blends were about the same or only increased slightly above the burn time of the neat base fuel. The ignition lag results show that halons are reasonably effective in preventing fire, but the burn time results suggest that halons are required in higher concentrations to extinguish a well-established fire. The effects of halons on established fires are explored later in the tests conducted to extinguish pool fires with halon sprays.

Figs. 8 through 13 show how the ignition lag increases for the 14 halons tested in Jet A. Figs. 8 through 10 show plots of ignition lag versus the weight percent halon in Jet A. Figs. 11 through 13 show similar plots of the ignition lag versus the relative concentration of halon in Jet A. The relative concentration is the weight percent halon divided by the weight percent halon required to prevent ignition of Jet A in the closed-cup flash-point test. Note that the halons have been split up into three groups dependent on the weight percent of halon required to prevent ignition in the closed-cup flash-point test. Group I includes those halons that required less than 1.5 wt% halon, Group II includes those that required from 1.6 to 3.0 wt% halon, and Group III includes those that required more than 3.1 wt% halon.

On examining the results in Figs. 8 through 10, it is seen that the Group I halons are most effective on a weight percent basis, but their effectiveness tends to increase rather slowly as their weight percent concentration is raised. Note that this statement is true for all the Group I halons

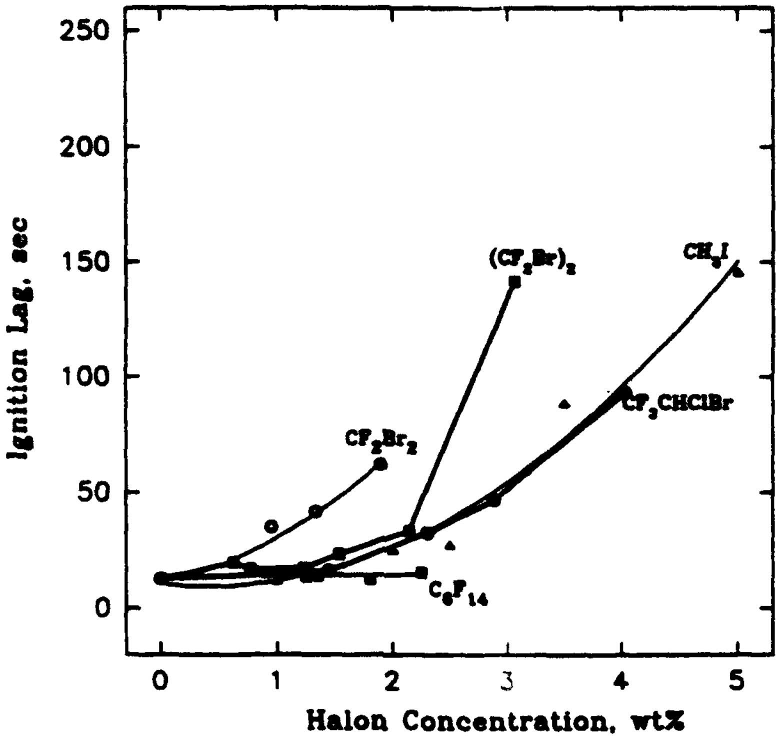

Figure 8. The dependence of ignition lag on weight percent halon in Jet A for the Group I halons

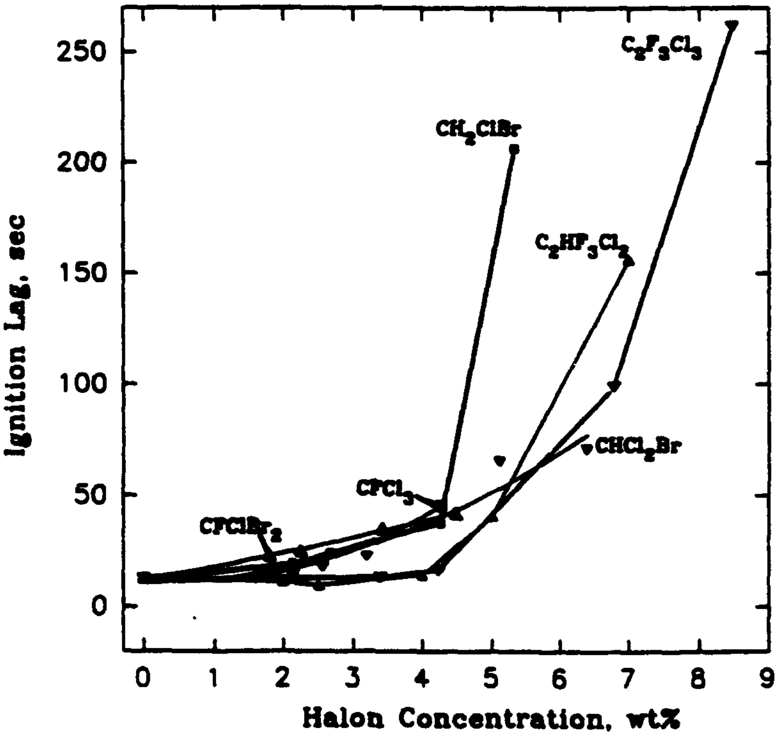

Figure 9. The dependence of ignition lag on weight percent halon in Jet A for the Group II halons

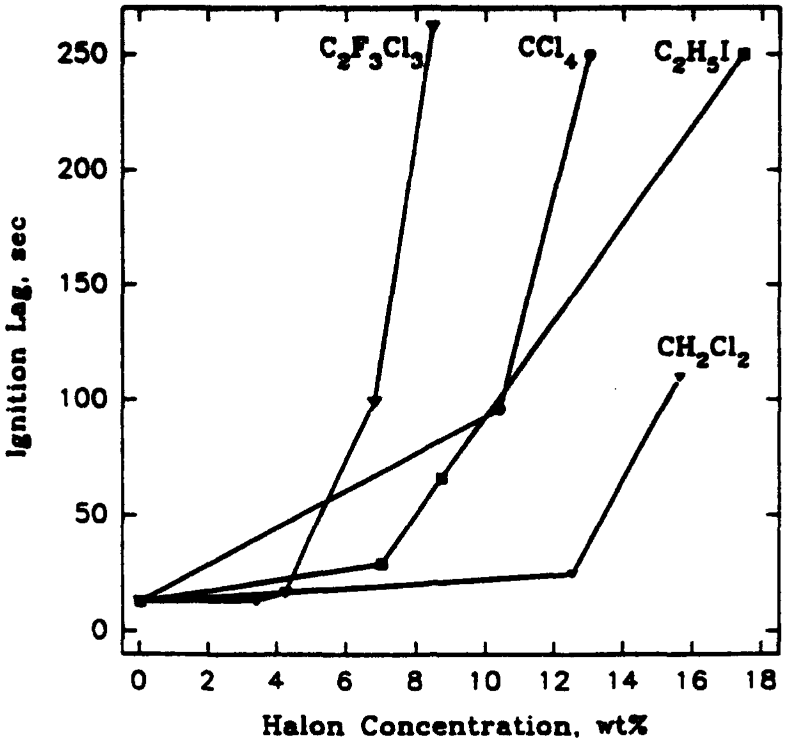

Figure 10. The dependence of ignition lag on weight percent halon in Jet A for the Group III halons

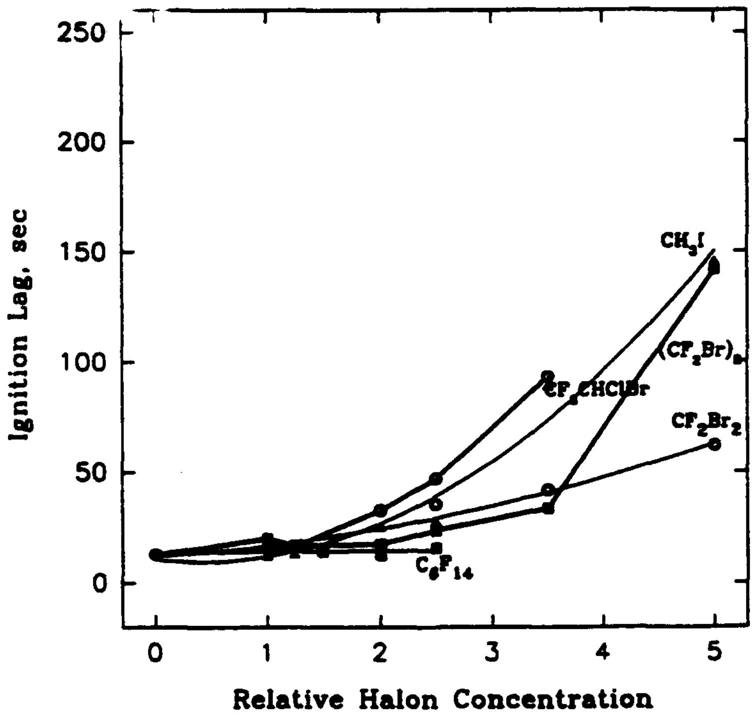

Figure 11. The dependence of ignition lag on the relative concentration of halon in Jet A for the Group I halons

(Note: Relative concentration is the absolute concentration divided by the halon concentration required to prevent ignition in the closed-cup flash-point apparatus.)

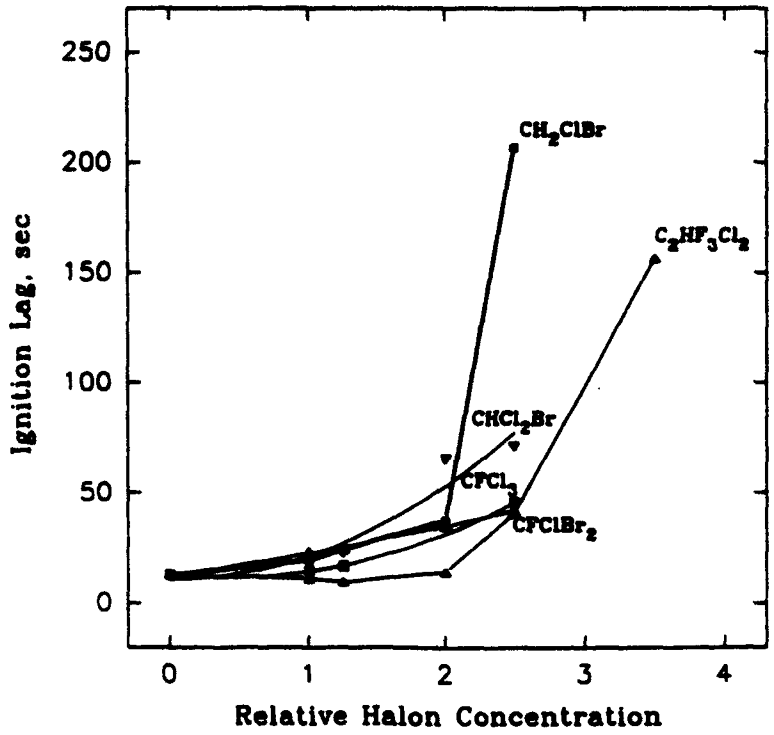

Figure 12. The dependence of ignition lag on the relative concentration of halon in Jet A for the Group II halons

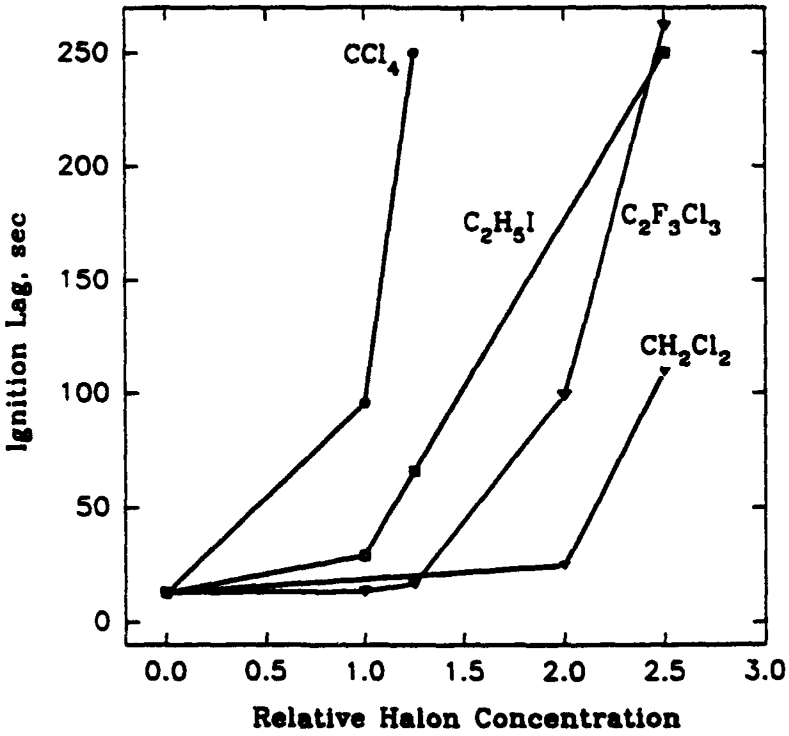

Figure 13. The dependence of ignition lag on the relative concentration of halon in Jet A for the Group III halons

except perfluorohexane, which did not show any increase in effectiveness with concentration. Figs. 9 and 10 show that the Group II and III halons require a higher weight percent to start with, but their effectiveness tends to increase more rapidly with concentration. Figs. 11 through 13 show this effect more clearly on the basis of relative concentration. Note that the effectiveness of the Group III halons increases more rapidly with the relative halon concentration than the Group II halons and, in turn, the Group II halons increase more rapidly than the Group I halons.

The above may be explained in terms of the absolute concentration of halon in the fuel. For the Group III halons, the concentration gradient across the liquid-vapor interface is the highest, so the mass diffusion rate of halon into the vapor space is also the greatest. When the weight percent of the Group III halons is doubled, there is a substantial increase in the mass diffusion of halon from the liquid phase into the vapor phase. On the contrary, when the weight percent of the Group I halons is doubled, there is very little increase in mass diffusion rate because the absolute concentration in the liquid phase has not changed significantly. These results indicate that the rate of mass diffusion of halon in the liquid phase to the vapor phase is an important parameter in determining the effectiveness of halons in preventing the ignition of fuel spills.

The effect of mass diffusion appears to be particularly important in the use of perfluorohexane. The results in TABLES 5 and 6 show that in the concentration range of 0.9 to 2.35 wt%, perfluorohexane has no inhibiting effect on flame spread over jet fuel. This effect is also illustrated in Figs. 8 through 13 in which the ignition lag is plotted against the respective absolute and relative halon concentrations. The results were somewhat of an enigma because the closed-cup flash-point tests showed that only 0.9 wt% of perfluorohexane was sufficient to impede ignition of both Jet A and the JP-4/Jet A blend.

In the closed-cup flash-point test, the halon/fuel vapor above the liquid fuel is confined so the concentration of halon vapor can build up to its equilibrium value. However, in an open pool, the halon vapor that enters the vapor space above the liquid fuel tends to disappear into the surrounding atmosphere because of convection and mass diffusion. If the rate of halon transport from the liquid phase to the vapor phase is slow compared to the rate at which the halon disappears into the surrounding atmosphere, the concentration of halon in the fuel/air mixture above the pool is going to be greatly diminished. Because perfluorohexane has a relatively high molecular weight, its mass diffusion coefficient is very small. Therefore, its transport rate out of the liquid phase is expected to be much slower than that of other lower molecular weight halons.

While perfluorohexane may be an effective fire-extinguishing agent in some situations, it seems to be relatively ineffective in preventing fuel spill fires. Because of its small mass diffusion coefficient and limited solubility in jet fuel, its concentration in the spilled fuel may never reach a level high enough to prevent ignition.

C. Spray Tests

Experiments were performed to determine a method of evaluating the effect of halon sprays on pool burning. In the first experiment, a halon spray was directed at approximately a 45-degree angle toward a burning pool of Jet A fuel. Three agents--carbon tetrachloride, Halon 123 (CF_3CHCl_2), and perfluorohexane (C_6F_{14})--were examined. Upon trying several spray nozzles of different flow rates, it was found that a relatively high flow rate of halon was required to extinguish the fire. To extinguish a pool fire in a 21.6- × 21.6- × 3.7-cm (8.5- × 8.5- × 1.5-in.) pan, a 76-liter/hr (20-gal./hr) fuel spray nozzle operating at differential pressure of 50 psi was utilized. With carbon tetrachloride, the fire could be extinguished in less than 2 seconds. Using the same spray conditions, Halon 123 extinguished the fire in approximately 5 seconds. Again, using the same conditions, it was found that perfluorohexane would not extinguish the fire.

In view of the results from the first experiment, a revised apparatus and test procedure were developed to determine the effectiveness of halon sprays in extinguishing pan fires. In this test, a burning pool of Jet A fuel contained in a 21.6- × 21.6- × 3.7-cm (8.5 × 8.5 × 1.5-in.) pan is extinguished by a halon spray directed onto the fire with an overhead spray nozzle positioned above the center of the pan. The halon sprays were produced by hollow cone spray nozzles ranging in flow rates from approximately 8 to 32 liter/hr (2 to 8 gal./hr). These flow rates are achieved with a differential nozzle pressure of 100 psi.

Preliminary tests performed with the 32-liter/hr (8-gal./hr) nozzle were made using carbon tetrachloride, Halon 123, and perfluorohexane. The halon effectiveness was gauged by the amount of time required to extinguish the fire. The extinguishment times for carbon tetrachloride, Halon 123, and perfluorohexane were 2, 4, and 4 seconds, respectively. Carbon tetrachloride was slightly more effective than Halon 123 and perfluorohexane.

Because the above test procedure seemed to be incapable of discerning among the various halons examined, a new test procedure to examine flame extinguishment with halon sprays was tried. In this test, a burning pool of Jet A fuel contained in a 21.6- × 21.6- × 3.7-cm (8.5- × 8.5- × 1.5-in.) pan is extinguished by a halon spray directed onto the fire with an overhead spray nozzle positioned about 10 inches above the center of the pan. The halon sprays were produced by hollow cone spray nozzles ranging in flow rates from 4 to 32 liter/hr (1 to 8 gal./hr). These flow rates were achieved with a differential nozzle pressure of 100 psi. The test procedure was to reduce the halon flow rate by changing from a 32-liter/hr (8-gal./hr) nozzle to a 28-liter/hr (7-gal./hr) nozzle and so forth until the spray would no longer extinguish the fire. The time required to achieve extinguishment was also recorded. Halon 123 (CF_3CHCl_2), perfluorohexane (C_6F_{14}), and trichloroethane (CH_3CCl_3) were examined.

With perfluorohexane, extinguishment was achieved within three seconds using the 32-, 28-, 24-, 20-, 16-, and 10-liter/hr (8-, 7-, 6-, 5-, 4-, and 2.5-gal./hr) nozzles. The fire could not be extinguished using nozzles with flow rate capacities of less than 10 liter/hr (2.5 gal./hr). Similar results were obtained for Halon 123. Trichloroethane was tested because the flash-point tests and flame-spread experiments showed it to be very ineffective compared to Halon 123. The tests showed that trichloroethane sprays produced by the 8-, 7-, 6-, and 5-gal./hr nozzles extinguished the fire within 3 seconds. Nozzles with capacities below 5 gal./hr would not extinguish the fire. Since the flash point and flame propagation tests have shown that the fire-extinguishing ability of Halon 123 is superior to that of trichloroethane, it was concluded that the pool-burning procedure needs further analysis to determine why this reversal in relative effectiveness was observed.

VI. CONCLUSIONS

Several halons were tested to determine their effectiveness in preventing the ignition of jet fuel spills. The measurements consisted of the closed-cup flash-point test, a pool ignition and flame spread test, and a spray-extinguishment test. Except for the latter, the objective of these tests was to determine the effectiveness of halons when they are dissolved in the fuel.

It was concluded from the flash-point tests that halon effectiveness was strongly dependent on halon composition and boiling point. The halon effectiveness, ε, was measured as the reciprocal of the mole percent of halon dissolved in the fuel. A correlation of the measured ε's with the physical and chemical properties of the halons showed that the effectiveness was exponentially dependent on the boiling point of the halon, proportional to the number of chemical bonds in the halon, and proportional to the numbers of H, F, Cl, Br, and I atoms in the halon molecule. It was concluded from the results of the correlation that halons composed of Cl, Br, and I atoms were respectively 1.23, 15.19, and 21.35 times more effective than those composed of F atoms. The presence of H atoms had a negative effect on the ability of the halon to prevent ignition of jet fuel.

Experiments on open-pool ignition and flame spread showed that to prolong ignition for more than a minute, the halon concentration had to be substantially higher than that required to prevent ignition in the closed-cup flash-point test. The halons had a substantial effect on ignition lag, but little or no effect on the burn-time or flame-spread rate. The absolute concentration of halon in the fuel greatly influenced the effectiveness of the halon in raising the ignition-lag time. This fact led to the conclusion that mass transport of halon from the liquid phase to the gas phase was very important in open-pool burning. While halons such as perfluorohexane are very effective in extinguishing fires in gas phase applications, they are rendered ineffective when mixed in the fuel because they have relatively small coefficients of mass diffusion. For this reason, it is important to consider the nature of the application when halons are used in the prevention and extinguishment of fires.

All of the 21 halons examined in this study were soluble in hydrocarbons in sufficient quantities to prevent ignition of jet fuel in the closed-cup flash-point test. In fact, most of the halons examined were completely miscible in jet fuel. Perfluorohexane was the only halon found to have very limited solubility in jet fuels. This limited solubility renders perfluorohexane alone essentially ineffective in preventing pool fires since it is required in relatively high concentrations in this application.

Although most of the halons examined were highly soluble in jet fuel, their solutions were far from being ideal. It was concluded that Raoult's law could not be assumed in calculating the partial pressure of the halon vapor blanketing the liquid fuel.

VII. RECOMMENDATIONS

This research identified mechanisms in fuel ignition and flame propagation and inerting/extinguishing agents' effectiveness in preventing pool burning. Future work would apply this information in developing suitable agent/agent dispersal schemes. Since results of the flash-point testing using perfluorohexane and full-scale ground vehicular tests indicated that this compound is extremely effective in preventing ignition of heated fuels, methods to enhance its effectiveness in controlling pool burning should be pursued. It appears that the main problem in preventing flame propagation is lack of agent solubility with hydrocarbon fuels. The density of perfluorohexane is approximately twice the hydrocarbon fuel. Therefore, some methods to prevent the agent from sinking to the bottom, thus allowing continued surface burning of the fuel, should be developed. The following concepts seem feasible and should warrant additional investigation:

A. Enhanced Surface Inerting (Halons/Surfactant)

The same principle of surfactant solubilization of two insoluble materials successfully developed for fire-resistant diesel fuel would be pursued. A surfactant should be identified or developed that would allow the agent to instantly solubilize to the surface of the spilled fuel, thus providing a ready source of inerting vapor when the surface is exposed to some ignition source. There are many surfactants today that solubilize polar solvents, and, in this case, the perfluorohexane acts as a quasipolar material, in terms of hydrocarbon solubility. This addition of a diluting or extending agent may reduce the volume of agent and provide for better dispersion of the agent. This concept utilizes a film-forming surfactant that would not be rigid and would flow with spilled fuel as it spread after impact.

The fuel trough could be used as the fuel container with ignition source. The agent mixtures could be flowed and/or sprayed onto the fuel surface. Testing could be done with and without fire. Additional experiments should use flowing fuel to investigate the mixing/loss phenomena. Fuel security would be indicated by the agent concentration spatial distribution with time. Fuel security would also be indicated by conducting a burnback test whereby a small area of the trough would be scooped clean of the agent mixture and ignited by a flame to see burn progression against the surface-protecting layer. Tests using an initial fire would provide the worst-case situation since additional agent would be lost during fire suppression and high-heat vaporization. Therefore, necessary application rates would be determined using fire experiments, whereas the simpler nonfire tests would be more conveniently used for all other measurements.

B. Enhanced Surface Inerting (H_2O/Surfactant/Halon)

Surface inerting is desirable over total fuel inerting to provide high aircraft-weight efficiency. A concern for surface inerting is the movement of the fuel on the ground, which may cause mixing and loss of the internal layer to the subsurface, thereby exposing a flammable fuel surface. The concept of Aqueous Film-Forming Foam (AFFF) is to provide a thin layer of surfactant/water on the fuel surface to separate it from air. This "light water" concept similar to AFFF might be employed to keep from losing the halon into the subsurface. Similar to the parameter for foams, the drainage time indicates loss into the subsurface.

This approach uses the surfactant concentrate/water as the carrier to support halon at the upper surface of the fuel. Initial trials would involve the addition of halons with various boiling points around the initial distillation temperature and flash point of the fuel of interest. The mixtures of the concentrate with water and with halon would form the solution for application. It is envisioned that the bubbles would provide for even (efficient) distribution of the halon/surfactant. The application mixing and the drainage provide for mixing with the upper surface of the fuel to inert it. Temporal measurements of agent concentration above and below the liquid fuel surface would indicate the performance.

C. Enhanced Surface Inerting (H_2O/Surfactant)

In the previous approach, halon was added to AFFF concentrate as a simple initial trial to induce "light halon-type agent" action to reduce the loss of halon to the subsurface. For comparative purposes, just the surfactant/water solution should be run. This solution will provide a measure of the halon performance in the previous approach.

These tests would be run exactly the same as the previous approach, which used H_2O/surfactant/halon in fire and nonfire fuel trough tests. An additional method that can be used for visualization purposes would be to add a dye to the agent mixture and use a transparent fuel trough (pyrex or quartz) in order to see the mixing processes.

D. Encapsulated Halon

The approach to encapsulate halons in order to increase their effectiveness through reduction of vapor loss would appear to have some merit. The actual encapsulation process would not appear to be a major obstacle, and it could increase effectiveness by allowing better control over the dispersal process. If the encapsulating material had a low density, thus allowing the caplets to float on the fuel surface, this approach could offer some merit from the standpoint of easier cleanup since only that agent required to extinguish the fire, by heat activation of the shell, would be consumed.

E. Agent Ingestion

While data are not available to verify this belief, it is felt that a major ignition source would be fuel ingested into the engine at time of crash. Although suppression systems are already designed for engine nacelles, it is believed that these systems would be totally ineffective in a crash scenario. Perfluorohexane has been shown to be effective in controlling engine compartment fires. Thus, dispensing nozzles located strategically not only to treat spilled fuel in the area around the engine locations but also to direct sufficient inerting agent into the combustion air to eliminate ignition and burning of spilled fuel may provide protection from further engine relight and continued burning or other ignition sources.

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LIST OF ACRONYMS

AFFF - Aqueous Film-Forming Foam
BFLRF - Belvoir Fuels and Lubricants Research Facility (SwRI)
CFC - Chlorofluorocarbons
DOD - Department of Defense
FC - Perfluorinated Hydrocarbons
GWP - Global Warming Potential
HCFC - Hydrochlorofluorocarbons
HFC - Hydrofluorocarbons
HQDA - Headquarters, Department of the Army
PFH - Perfluorohexane
ODP - Ozone Depletion Potential
USAF - United States Air Force
USEPA - United States Environmental Protection Agency
UV - Ultraviolet

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