AFAPL-TR-71-93

×

IGNITION AND FIRE SUPPRESSION IN AEROSPACE VEHICLES

Joseph M. Kuchta Ralph J. Cato George H. Martindill Irving Spolan

Bureau of Mines PMSRC Report No. 4164

TECHNICAL REPORT AFAPL-TR-71-93

December 1971

APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED

NATIONAL TECHNICAL INFORMATION SERVICE Springfloid, Va. 22131

Air Force Aero Propulsion Laboratory Air Force Systems Command Wright-Patterson Air Force Base, Ohio

D FEB 28 1972 2.41 Ù 14

and the second second

NOTICES

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

Copies of this report should not be returned unless return is required by security considerations, contractual obligations, or notice on a specific document.



UNCLASSIFIED					
Security Classification DOCUMENT CONTROL DATA - R & D					
(Security classification of title, body of obstract and indexing annotation must be entered when the overall report is classified)					
Pittsburgh Mining and Safety Research Cen	nter	Uncl	CURITY CLASSIFICATION		
Bureau of Mines Pittsburgh, Pennsylvania 15213					
S REPORT TITLE					
Ignition and Fire Suppression in Aerospa	ce Vehicles				
 DESCRIPTIVE NOTES (Type of report and inclusive deles) Technical Report, 1 January 1970 to 30 No. 	ovember 1971	•			
Joseph M. Kuchta George H. Martind: Ralph J. Cato Irving Spolan	111				
December 1971	74. TOTAL NO. 01 38	PA6E5	76. NO OF REFS 7		
B. CONTRACT OR GRANT NO	B. CRISINATOR	REPORT NUME	CR(5)		
F33013-09-R-3002	No MORE AND				
3048					
Task No. 304807	this report)				
d.	AFAFL-TR-71-93				
10 DISTRIBUTION STATEMENT					
Approved for public release; distribution	unlimited.				
11 SUPPLEMENTARY NOTES	12 SPONSORING	APTO PTO	nity mulaion Laboratory		
	Wright-P	tterson Al	Base, Ohio 45433		
¹³ Assimilation: Several halogenated hydrocarbons sion suppressants for aircraft fuel tanks is ary ammunition. The inhibitors included Ha (CF2Br2), 1211 (CF2ClBr), and JO11 (CH2ClBr tion or propagation of n-pentane-air mixtur ploding wires, and an incendiary composition the ignition delays of the mixtures increased to 0.5 volume percent, except with inhibitor. With the exploding wire and indelays of the combustible mixtures were neglightions although the concentrations required ignitions. In another part of this work, large-scatchamber with Halon 1301 to determine its efficient for rapid extinguishment of cottor sheeting fires at loadings from 0.018 to 0, when the extinguishant was discharged with nozzle or a shower manifold. The highest rates; HF was use than HBr but less than CO. The toxic products (HF and HBr) occurred with the pagand burned at the highest rates; HF was use than HBr but less than CO. The toxic product for small-scale experiments with than Halon 1301 as an extinguishant.	were evaluat in which igni- lons 2402 ((c). Their ef- res was inves- on. With a h- bed greatly w th Halon 1011 cendiary igni- ligible and all inhibito ed were great ile experiment fectiveness ing mode. A (a sheeting, p 07 of/ft ³ . a dispersion per sheeting ially found is ist formation thange mode. A Halon 38 ((ed as posi- tions are 2F4Br2), if fectivenes tigated wi- eated play then the He which ware varied lift ors suppre- tion source varied lift ors suppre- tion source than in this were co and toxics percent l aper sheet Extinguish nozzle the which pro- n much high varied wi- in addit: 3Fg), which	sible ignition or explo- initiated by incendi- 1301 (CF3Br), 1202 as in retarding igni- 1th heated wires, ex- tinum wire at 2070°?, alon concentration was the least effective ces, the ignition ttle with inhibitor used the flame propa- a the heated wire onducted in a 216 ft3 Ity hazard in extin- Balon concentration was ting, and nylon-paper hing times were longer han with an open pipe t decomposition buced the largest firm pher concentrations ith preburn time, com- ion, similar data are the least effective		
DD 1004					

Unclassified Security Classification

and the second sec

UNCLASSIFIED Security Classification

INCLASSIFIED Security Classification

IGNITION AND FIRE SUPPRESSION IN AEROSPACE VEHICLES

Joseph H. Kuchta Ralph J. Cato George H. Martindill Irving Spolan

Approved for public release; distribution unlimited.

.

FOREWORD

This report was prepared by the Pittsburgh Mining and Safety Research Center of the U. S. Bureau of Mines under USAF Contract No. F33615-69-M-5002. The contract was initiated under Project 3048, "Fuels, Lubrication, and Hazards," Task 304807, "Aerospace Vehicle Hazard Protection." It was administered under the direction of the Air Force Aero Propulsion Laboratory, with Mr. Robert G. Clodfelter (SFH) acting as project engineer.

This report summarizes the work recently completed under this contract during the period 1 January 1970 to 30 November 1971.

Dr. Robert W. Van Dolah was the administrator for the U. S. Bureau of Mines and Messrs. Joseph M. Kuchta, Ralph J. Cato, George H. Martindill, Irving Spolan and John D'Auria actively participated in this work at the U. S. Bureau of Mines, Pittsburgh Mining and Safety Research Center, Bruceton, Pennsylvania.

This report was submitted by the authors November 1971.

This technical report has been reviewed and is approved.

BENITO P. BOTTERI Chief, Fire Protection Branch Fuels and Lubrication Division

ABSTRACT

Several halogenated hydrocarbons were evaluated as possible ignition or explosion suppressants for aircraft fuel tanks in which ignitions are initiated by incendiary ammunition. The inhibitors included Halons 2402 (C2F4Br2), 1301 (CF3Br), 1202 (CF2Br2), 1211 (CF2ClBr), and 1011 (CH2ClBr). Their effectiveness in retarding ignition or propagation of n-pentane-air mixtures was investigated with heated wires, exploding wires, and an incendiary composition. With a heated platinum wire at 2070°F, the ignition delays of the mixtures increased greatly when the Halon concentration was increased to 0.5 volume percent, except with Halon 1011 which was the least effective inhibitor. With the exploding wire and incendiary ignition sources, the ignition delays of the combustible mixtures were negligible and varied little with inhibitor concentration (0 to 10 percent). However, all inhibitors suppressed the flame propagations although the concentrations required were greater than in the heated wire ignitions.

In another part-of this work, large-scale experiments were conducted in a 216 ft³ chamber with Halon 1301 to determine its effectiveness and toxicity hazard in extinguishing Class A fires by the total flooding mode. A 6 percent Halon concentration was adequate for rapid extinguishment of cotton sheeting, paper sheeting, and nylon-paper sheeting fires at loadings from 0.018 to 0.07 oz/ft^3 . Extinguishing times were longer when the extinguishant was discharged with a dispersion nozzle than with an open pipe nozzle or a shower manifold. The highest concentrations of toxic decomposition products (HF and HBr) occurred with the paper sheeting which produced the largest fires and burned at the highest rates; HF was usually found in much higher concentrations than HBr but less than CO. The toxic product formation varied with preburn time, combustible loading, and the extinguisher discharge mode. In addition, similar data are presented from small-scale experiments with Halon 38 (C₃F₈), which is less effective than Halon 1301 (CF₃Br) as an extinguishant.

TABLE OF CONTENTS

....

.

	FAGE
INTRODUCTION	1
EXPERIMENTAL APPARATUS AND PROCEDURES	2
A. Ignition Suppressants for Fuel Tank Protection	2
1. Wire Ignition Experiments	2
2. Exploding Wire and Incendiary Ignition Experiments	3
B. Fire Suppression Techniques for Aerospace Vehicles	6
1. Large-Scale Experiments with Halon 1301	6
2. Small-Scale Experiments with Halon 38	9
RESULTS AND DISCUSSION	9
A. Ignition Suppressants for Fuel Tank Protection	9
1. Inhibitor Effectiveness in Wire Ignitions	9
2. Inhibitor Effectiveness in Exploding Wire and Incendiary Ignitions	16
B. Fire Suppression Techniques for Aerospace Vehicles	21
1. Characterization of Burning in Fire Extinguishing Experiments	21
2. Toxic Product Formation with Halon 1301	28
3. Toxic Product Formation with Halon 38	35
CONCLUSIONS	35
RECOMMENDATIONS	38

ILLUSTRATIONS

FIGURE		PAGE
1.	Wire ignition apparatus	4
2.	Incendiary powder igniter assembly	5
3.	Sketch of experimental setup for fire extinguishing experiments in 6-foot cubical chamber (216 ft ³)	7
4.	Effect of added nitrogen on ignition delay of stoichio- metric n-pentane-air mixtures (1 atm) ignited with a platinum wire (0.016-inch diameter by 1-1/4-inch long) at 2050°F	10
5.	Variation of ignition delay with Halon concentration for ignitions of stoichiometric n-pentane-air mixtures (1 atm) and various Halons with a platinum wire (0.016- inch diameter by 1-1/4-inch long) at 2070°F	13
6.	Effect of initial wire temperature on the ignition delay of stoichiometric n-pentane-air mixtures (1 atm) with 0.5 volume percent Halon 1301	14
7.	Effect of fuel concentration on the ignition delay of n-pentane-air mixtures (1 atm) with 0.5 volume percent Halon 1301 (wire temperature - 2150°F)	15
8.	Variation of initial rate of pressure rise with Halon concentration for ignitions of stoichiometric n-pentane- air mixtures (1 atm) and various Halons with a Pyrofuze wire (0.005-inch diameter by 1-1/4-inch long)	19
9.	Variation of initial rate of pressure rise with Halon concentration for ignitions of stoichiometric n-pentane- air mixtures (1 atm) and various Halons with an incen- diary powder (0.17 gm)	20
10.	Variation of initial rate of pressure rise with Halor 1301 concentration for ignitions of stoichiometric n-pentane- air mixtures (1 atm) with an incendiary powder, Pyrofuze wire, and Chromel fuse wire	22
11.	Effect of total pressure on the initial rate of pressure rise in exploding wire ignitions with stoichiometric n-pentane-air mixtures containing 4, 6, and 8 percent Halon 1301; (0.005-inch diameter by 1-1/4-inch long Pyrofuze wire)	23

ILLUSTRATIONS (Cont'd)

FIGURE

PAGE

12.	Pressure rise versus time for the burning of paper and cotton sheeting (0.035 oz/ft^3) in air on single and dcuble burning racks in a 216 ft ³ chamber (1 atm)	24
13.	Peak pressure rise and weight loss of combustible versus preburn time in extinguishing cotton sheeting fires with 6 percent Halon 1301 in air at a combustible loading of 0.035 oz/ft ³ . (Pipe nozzle, 350 psig discharge pressure)	26
14.	Peak pressure rise and weight loss of combustible versus preburn time in extinguishing paper and nylon (65 percent)- paper (35 percent) sheeting fires with 6 percent Halon 1301 in air at a combustible loading of 0.035 oz/ft ³ . (Pipe nozzle, 350 psig discharge pressure)	· 27
15.	Hydrogen bromide and hydrogen fluoride concentrations (2 sampling times) versus preburn time in extinguishing cotton sheeting fires with 6 percent Halon 1301 in air at a combustible loading of 0.035 oz/ft ³ . (Pipe nozzle, 350 psig discharge pressure)	30
16.	Hydrogen bromide and hydrogen fluoride concentrations (2 sampling times) versus preburn time in extinguishing paper sheeting fires with 6 percent Halon 1301 in air at a com- bustible loading of 0.035 oz/ft ³ . (Pipe nozzle, 350 psig discharge pressure)	31
17.	Hydroger bromide and hydrogen fluoride concentrations (2 sampling times) versus preburn time in extinguishing nylon (65 percent)-paper (35 percent) sheeting fires with Halon 1301 in air at a combustible loading of 0.035 oz/ft ³ . (Pipe nozzle, 350 psig discharge pressure)	32
18.	Carbon monoxide concentrations (2 sampling times) versus preburn time in extinguishing cotton, paper, nylon (65 percent)-paper (35 percent) sheeting fires with Halon 1301 in air at a combustible loading of 0.035 oz/ft ³ . (Fipe nozzle, 350 psig discharge pressure)	34
19.	Hydrogen bromide and hydrogen fluoride concentrations versus combustible loading in extinguishing cotton sheet- ing fires with 6 percent Halon 1301 by various discharge modes. (350 psig discharge pressure)	36

vii

TABLES

PAGE

TABLE

Ι.	Physical properties of Halons	2
11.	Minimum ignition delay data from wire ignition experi- ments with various Halons (2402, 1202, 1301, 1211 and 1011) and stoichiometric n-pentane-air mixtures at 1 atmosphere pressure	12
111.	Pressure rise data from exploding wire ignition experi- ments with various Halons (2402, 1202, 1301, 1211, and 1011) and stoichiometric n-pentane-air mixtures at 1 atmosphere pressure	17
IV.	Pressure rise data from incendiary ignition experiments with various Halons (2402, 1202, 1301, and 1211) and stoichiometric n-pentane-air mixtures at atmospheric pressure	18
V.	Extinguishing times and amounts of combustible and oxygen consumed in fire extinguishing experiments with Halon 1301 (6 percent) and cotton, paper and nylon (65 percent)-paper (35 percent) sheeting in a 216 ft ³ test chamber	29
VI.	Toxic limits of product gases or vapors	33
VII.	Data from fire extinguishing experiments with perfluoro- propane (Halon 38) and cotton sheeting in a 12 ft ³ cylindrical chamber	37

INTRODUCTION

This report is the last of a series of four reports generated under Contract F33615-69-M-5002 "Investigation of Flight Vehicle Materials, Fire Characteristics and Fire Explosion Suppression Techniques." Previous reports dealt with flame arrestor materials for fuel tank explosion protection¹/ and the ignition of various aircraft fluids by hot surfaces under simulated flight conditions.²/ The third report³/ treated Halon 1301 as a total flooding extinguishing agent and relates directly to the current report. The experimental work herein reported was divided into two separate parts: (1) Ignition Suppressants for Fuel Tank Protection and (2) Fire Suppression Techniques for Aerospace Vehicles.

The work pertaining to Part 1 was initiated to assess the effectiveness of various chemical flame inhibitors as possible ignition or explosion suppressants for aircraft fuel tanks in which ignitions are initiated by high temperature external sources, such as incendiary ammunition. To be effective, the inhibitor must increase the ignition delay of the fuel vapor-air mixture to a value that will exceed the "effective lifetime" of the incendiary, or suppress the resultant flame propagation to prevent excessive fuel tank pressures. A brief literature search revealed that, while many chemical compounds are capable of acting as inhibitors, volatile organic halides containing bromine or iodine and alkali metal salts appear to be the most effective for hydrocarbon vapor-air mixtures. The inhibitors in the present work were limited to halogenated hydrocarbons such as Halons 2402 (C₂F₄Br₂), 1301 (CF₃Br), 1202 (CF₂Br₂), 1211 (CF₂ClBr), and 1011 (CH₂ClBr). Table I lists some of their physical properties. An inerting agent (nitrogen) was also included in this work for comparison. The inhibitors were evaluated by determining their effectiveness in retarding the ignition or propagation of n-pentane vapor-air mixtures initiated by heated wires, exploding wires, and a representative incendiary source. Ignition delays and rates of pressure rise were used to define the order of inhibitor effectiveness.

- 1/ Kuchta, J. M., R. J. Cato, and W. H. Gilbert, Flame Arrestor Materials for Fuel Tank Explosion Protection, AFAPL-TR-70-40, July 1970.
- 2/ Strasser, A., N. Waters, and J. M. Kuchta, Ignition of Aircraft Fluids by Hot Surfaces Under Dynamic Conditions, AFAPL-TR-71-86, November 1971.
- <u>3</u>/ Martindill, G. H., I. Spolan, and J. M. Kuchta, Fire Suppression for Aerospace Vehicles, AFAPL-TR-70-39, July 1970.

	Formula	Mol. Wt.	Boiling Point, °F	Vapor Density (70°F) lb/ft ³	Vapor Pressure (70°F) psia	Approximate Lethal Concentration ^a ppm
Halon 2402	CoFABro	260	116		5.6	1600 ^b /
Halon 1301	CF3Br	149	-72	0.39	215	14.000 ^b /
Halon 1202	CF2Br2	210	76	0.54	13	1850 <u>b</u> /
Halon 1211	CF2BrC1	166	21	0.43	35	7650 <u>b</u> /
Halon 1011	CH2BrC1	130	153		2.8	4000 <u>b</u> /

TABLE I. - PHYSICAL PROPERTIES OF HALONS.

a/ Decomposed vapor at approximately 1470°F.

b/ Engibous, D. L. and T. R. Torkelson, A Study of Vaporizable Extinguishants, WADC TR-59-463, January 1960, 116 pp.

Part 2 of this report is concerned with the semifull-scale evaluation of fire suppression systems and techniques that may be suitable against Class A fires in advanced aircraft, such as the F-111. Previous work² was limited to cotton sheeting fires that were extinguished with Halon 1301 (CF₃Br) by the total flooding mode in a 6-foot cubical chamber; data were obtained on the effectiveness of this agent and on the toxic decomposition products formed in extinguishing the fires with a commercial extinguisher discharging a solid Halon jet against the chamber walls. Similar data are presented in this report from extinguishing experiments with other total flooding discharge modes and other combustibles, such as paper sheeting and nylon-paper sheeting. Results of small-scale experiments with Halon 38 (C₃F₈), a less effective agent than Halon 1301, are also discussed.

EXPERIMENTAL APPARATUS AND PROCEDURE

A. Ignition Suppressants for Fuel Tank Protection

1. Wire Ignition Experiments

Ignition delay data were obtained with the wire ignition apparatus shown in Figure 1. This apparatus was equipped with a 75.7 in³ glass reaction vessel, 4 inches in diameter by 6 inches long, into which the fuel vapor-air-inhibitor mixture was rapidly introduced and centrally ignited by a heated platinum wire, 0.016-inch diameter by 1-1/4 inches long. In an experiment, the vessel was initially evacuated and the platinum wire was electrically heated to a predetermined temperature by a constant current power supply; the surface temperature of the wire was measured by an optical pyrometer or an infrared radiation pyrometer. The test mixture was then introduced as rapidly as possible (≤ 40 milliseconds) from the pressurized storage vessel at 60 psig by use of a quick-acting solenoid valve. The reaction vessel was instrumented with a strain-gage pressure transducer for measuring the pressure development and a photodiode for detecting the onset of flame and the change in wire luminosity or temperature; their electrical outputs were fed to an oscilloscope equipped with a camera. To protect the glass reaction vessel, it was fitted with an explosion relief diaphragm which ruptured when the pressure was over 20 psig. The ignition delay of the test mixture was determined from the pressure rise and wire luminosity measurements obtained in each experiment. Here, ignition delay was defined as the interval from the time the mixture was introduced into the vessel, as evidenced by a change in wire temperature, to the instant when flame was detected.

The wire ignition experiments were performed with n-pentane-air mixtures containing various concentrations of the Halon inhibitors (0 to 10 volume percent) at a mixture temperature of $75^{\circ} \pm 10^{\circ}$ F and total pressure of 5 to 20 psia. Most experiments were made with near stoichiometric n-pentane-air mixtures and an initial wire temperature of $2070^{\circ} \pm 30^{\circ}$ F, although other fuel concentrations and wire temperatures were also investigated. In all experiments, the wire was coated with a ceramic material to minimize possible catalytic effects.

2. Exploding Wire and Incendiary Ignition Experiments

The apparatus used in this portion of the work was basically the same as that shown in Figure 1, except for a few minor modifications. In these experiments, the test mixtures were added to the reaction vessel prior to initiating the ignition energy sources. The ignition sources consisted of exploding Pyrofuze* wires, 0.005-inch diameter by 1-1/4 inches long, and small charges (0.17 gm) of an incendiary powder composition (IM-11), a 50-50 mix of barium nitrate and magnesium-aluminum powder. Figure 2 shows a photograph of the incendiary igniter assembly, which was fabricated from a Conax fitting, with a 7/16 inch bore and equipped with a 1/4-inch diameter electrode. The incendiary was loaded in the annular space (3/32-inch wide by 3/64-inch long) within the Conax fitting and secured with a 1 mil aluminum diaphragm. The incendiary source was mounted at the bottom of the test vessel, whereas the exploding wire was centrally mounted, as in the wire ignition experiments. Both ignition sources were initiated by passing an electrical discharge of a 1 microfarad capacitor, charged to 5 kilovolts, through the igniter materials. Chromel C fuse wires (nickel-chromium-iron alloy) were also used as an ignition source for comparison. Here, pressure rise measurements were generally relied upon to evaluate the ignition suppression

* Reference to specific trade names is made to facilitate understanding and does not imply endorsement by the Bureau of Mines.





FIGURE 2. - Incendiary powder igniter assembly. (Incendiary cavity - 3/64 in. long annular space, 7/16 in. outer diameter by 1/4 in. inner diameter).

effectiveness of the Halon materials since the ignition delays of most of the n-pentane-air-Halon mixtures were minimum with such high temperature sources. The maximum effective temperatures of the incendiary powder and Pyrofuze wire are reported to be greater than 4000° and 5000°F, respectively. The Chromel C wire has a melting point of approximately 2460°F, but its temperature on firing was obviously higher, since the wire was vaporized and appeared to be largely consumed.

B. Fire Suppression Techniques for Aerospace Vehicles

1. Large-Scale Experiments with Halon 1301

Fire extinguishing experiments with Halon 1301 were conducted in a 6 ft cubic chamber (216 ft^3) designed to withstand a pressure of approximately 15 psig. A sketch of the experimental setup is shown in Figure 3. The combustible sheeting was normally mounted on a rectangular rack suspended in the center of the chamber and ignited by a nichrome coil along the entire bottom edge of the specimen. After a predetermined burning period, the burning was extinguished with the Halon agent by the total flooding mode using various discharge systems. The test chamber was instrumented for monitoring pressure and temperature changes and for sampling combustion products during a run. The chamber was also equipped with 6-inch glass ports for observation and for obtaining motion picture records of the burning and extinguishing.

The combustibles included cotton sheeting (5.1 oz/yd^2) , a 2-ply "Sanidrape" paper sheeting (2.1 oz/yd^2) , and a nylon sheeting (1.7 oz/yd^2) which was burned in combination with the paper. Most experiments were made at a combustible loading of 0.035 oz/ft^3 in the chamber, using one or two !/urning racks. For the cotton material, this loading (7.62 oz)was realized by the use of two sheets measuring 36 by 27 inches, as compared to four sheets measuring 36 by 42 inches for the 2-ply paper sheeting. To vary the loading, the number of sheets was increased or decreased. When two racks were employed, they were usually spaced about one foot apart and the combustible was equally divided between them.

Because of the low melting point of nylon, it could not be ignited by the same method used with the cotton and paper specimens. Generally, contact with the heated coil was lost before ignition could occur. Also, although ignition could be achieved by wrapping the igniter coil with a layer of cotton gauze, the burning of the vertically mounted specimen was erratic and self-extinguishment occurred after only 60 weight percent had either burned or melted away. Therefore, to obtain reproducible burning, various combinations of paper sheeting sandwiched between nylon sheeting were investigated. A combination of 65 percent nylon and 35 percent paper appeared to give the most uniform burning and was used for the extinguishing tests. To provide a combustible loading of 0.035 oz/ft³ with this combination, two 36- by 28-inch sheets of nylon and one of paper were required for burning on a single rack.



FIGURE 3. Sketch of experimental setup for fire extinguishing experiments in 6-foot cubical chamber (216 ft³).

Three extinguisher discharge systems were used in the present study. In the first, the Halon was discharged from a 378 in³ spherical extinguisher bottle (Walter Kidde) mounted near one corner of the chamber, as shown in Figure 3. The bursting of a retaining disc by a pyrotechnic charge released the agent through a 1-1/2-inch pipe nozzle to impinge on a chamber wall at a 45° angle, 20 inches below the top of the chamber. Sufficient Halon was injected to form either a 6 volume percent (4.8 lb) or a 10-volume percent (8.0 lb) mixture in the chamber. The total pressure propelling the extinguishant was 220 psig (the vapor pressure of Halon 1301 at 75°F), but most experiments were made at a discharge pressure of 350 psig by the use of added nitrogen. For a 4.8 lb Halon charge at 350 psig, the initial and average rates of discharge were approximately 12 and 6 lb/sec, respectively.

In the second discharge system, the 378 in³ commercial extinguisher was connected to a shower manifold consisting of two 1-inch tubes, each with two rows of 1/4-inch diameter holes. These tubes were placed two feet apart and mounted in the horizontal plane at the top of the burning rack. With this arrangement, the extinguishant was discharged downward on both sides of the burning specimen; the total dispersion angle was 60° for each tube. The third Halon distribution system utilized a cylindrical extinguisher bottle (Fenwal), which measured 5 inches in diameter and 18 inches in length and had a capacity of 310 cubic inches. This bottle is designed to release its contents abruptly through a 3-inch diameter outlet that is equipped with a dispersion head having 31 holes of about 3/8-inch diameter; the discharge was effected by firing a detonator within the bottle which ruptured a 3-inch scored diaphragm. The bottle was mounted in the chamber to discharge against the walls, as in the experiments with the other commercial extinguisher.

To obtain samples of the gaseous products during a run, a sampling port was placed 6 inches below and 6 inches away from the specimens and connected to a set of four sample bottles. Because of the highly corrosive nature of the fluorides in the gaseous products, acrylic sampling containers were used. Evacuation of the bottles and sampling of combustion products were remotely controlled by stainless steel solenoid valves. Sampling sequence and firing of the pyrotechnic charge were regulated by a program timer. Gas samples were taken at various time intervals, depending upon the experiment. In experiments with extinguishment, at lease one sample was taken 5 seconds after the Halon discharge and another 3 to 4 minutes later when the system was essentially at equilibrium.

Conventional gas chromatographic techniques using a molecular sieve column were employed to analyze for oxygen, nitrogen, carbon monoxide, hydrogen, and methane. Carbon dioxide was analyzed on a Poropak Q column and Halon 1301 on a Chromosorb P column with Silicone 200. The hydrogen bromide and hydrogen fluoride were absorbed into water from the collected gas samples and were determined electrometrically using specific ion

electrodes. $\frac{4.5}{}$ An expanded scale meter was used to read the potential between the specific ion electrode (bromide or fluoride), and a calomel reference electrode. The weight of the bromide or fluoride absorbed from the gas sample was then read from a previously prepared calibration curve relating micrograms versus emf for each electrode. The weight was then converted to vapor volume concentration for the sample as collected.

2. Small-Scale Experiments with Halon 38

A few experiments were also conducted in a 12 ft³ cylindrical chamber 2-ft diameter by 4-ft high, to evaluate perfluoropropane (Halon 38) in extinguishing cotton sheeting fires. The cotton sheeting specimens were 16 inches long by 4 inches wide and were suspended in the center of the chamber; a double layer represented a loading of 0.035 oz/ft³ and four layers corresponded to 0.070 oz/ft³. Ignition was initiated along the bottom edge of the specimen and extinguishment was investigated using the total flooding mo⁻ and premixed mixtures of the Halon and air. The extinguishing effectiveness of the agent and the toxic product formation were determined as in the large-scale experiments.

RESULTS AND DISCUSSION

A. Ignition Suppressants for Fuel Tank Protection

1. Inhibitor Effectiveness in Wire Ignitions

Initially, wire ignition experiments were performed with n-pentane-airnitrogen mixtures at atmospheric pressure to obtain reference ignition delay data for comparison with the halogenated flame inhibitors. Figure 4 shows the ignition delay data obtained from runs with stoichiometric n-pentane (2.5 percent)-air mixtures containing 0 to 40 percent added nitrogen. The combustible test mixtures were examined with the initial temperature of the 0.016-inch diameter by 1-1/4-inch long platinum wire at 2050° ± 50°F. Two curves are drawn in Figure 4 to indicate the reproducibility of these data. Although the data display considerable scatter, the minimum ignition delays consistently increased with an increase in the inert concentration. The effect of added nitrogen was most pronounced when the concentration was increased from 20 to 40 volume percent; as noted, the minimum ignition delays increased from approximately 125 to 860 milliseconds over this range of nitrogen dilution. The high ignition delays with the addition of 40 percent nitrogen were expected, considering that only slightly higher inert concentrations are required to prevent the formation of flammable n-pentane-air-nitrogen mixtures.

5/ Srinivasan, K., G. A. Rechnitz, Activity Measurements With a Fluoride-Selective Membrane Electrode, Anal. Chem., Vol. 40, 1968, pp. 509-512.

^{4/} Frant, M. S., J. W. Ross, and J. M. Riseman, Ion-Selective Electrodes, American Laboratory, January 1969, pp. 14-22.



FIGURE 4. Effect of added nitrogen on ignition delay of stoichiometric n-pentane-air mixtures (1 atm) ignited with a platinum wire (0.016-inch diameter by 1-1/4-inch long) at 2050°F.

Corresponding ignition delay data from experiments with stoichiometric n-pentane-air mixtures and various Halon inhibitors are shown in Table II and Figure 5. Of the five Halon inhibitors examined, Halon 1011 appears to be the least effective and Halon 2402 the most effective as an ignition inhibitor, whereas the other Halons (1202, 1301, and 1211) rank about equal in their effectiveness and give intermediate ignition delays under these test conditions. According to the results, four of the Halons (2402, 1202, 1301, and 1211) were noticeably effective in increasing the ignition delay of the gas mixture when the inhibitor concentration was increased from 0.25 to 0.50 percent; Halon 1011 was an exception. Their minimum ignition delays at the 0.5 percent concentration varied from 1000 milliseconds for Halon 2402 to between 500 and 700 milliseconds for Halons 1202, 1301, and 1211; Halon 1011 concentrations greater than 0.75 percent appeared necessary to yield comparable ignition delays. In addition, the critical concentration for preventing ignition was slightly lower with Halon 2402 (0.75 percent) than with the other Halons (\geq 1.0 percent). These critical concentrations were lower than those reported for flame propagations of such mixtures in which a more severe ignition source was used. $\frac{6}{}$ As expected, all of the present Halon inhibitors were much more effective ignition suppressants than nitrogen, which acts as a diluent rather than a chemical inhibiting agent in the combustion process.

The effect of wire temperature (2000° to 2300°F) on ignition delay was determined for stoichiometric n-pentane-air mixtures with 0.50 percent Halon 1301. Halon 1301 was chosen for these experiments primarily because it is more widely used as a flame or explosion suppressant than the other materials. Figure 6 shows that the ignition delays increased abruptly when the initial wire temperature was reduced below 2100°F. Above this temperature, the minimum ignition delays were less than 50 milliseconds. At wire temperatures greater than 2300°F, the effectiveness of the Halon as an ignition inhibitor would tend to be practically negligible unless higher Halon concentrations (>0.5 percent) were present. Similar results would be expected with the other halogenated agents included in this study.

Ignition delays were not particularly sensitive to fuel concentration variations. Figure 7 shows the variation of the ignition delay of various n-pentane-air mixtures to which 0.5 percent Halon 1301 was added; the platinum wire temperature was $2150^{\circ} \pm 30^{\circ}$ F. The ignition delay data indicate that the effect of fuel concentration (1.8 to 5.0 percent npentane) is rather small, although the minimum values are higher with fuel-rich mixtures. These results are consistent with theoretical predictions in that the most incendive mixture occurs close to the stoichiometric (2.55 percent) fuel concentration for complete combustion.

6/ Purdue University, Final Report on Fire Extinguishing Agents, Contract W44-009-eng.507, Army Engrs. Res. and Dev. Labs., June 30, 1950.

	EXPERIMENTS WITH VARIOUS	HALONS (2402, 1202, 1301,		
	<u>1211 and 1011) AND STOICHIOMETRIC n-PENTANE-AIR</u>			
	MIXTURES AT 1 ATMOSPHERE	PRESSURE.		
	Platinum Wire (2070°F)	- 0.016 inch diam. by		
		1-1/4 inches long		
<u></u>				
	Added Halon,	Minimum Ignition Delay,		
	Vol. %	milliseconds		
Halon 2402	0	40		
	0.25	45		
	50	1000		
	75	No ignition		
	.,,,	No Ignición		
Halon 1202	θ	40		
	0.25	55		
	. 50	660		
	1.0	No ignition		
		0		
Halon 1301	0	40		
	0.25	45		
	. 50	590		
	1.0	No ignition		
		-		
<u>Halon 1211</u>	0	40		
	0.25	50		
	. 50	520		
	1.0	No ignition		
Halon_1011	0	40		
	0.25	40		
	. 50	65		
	. 75	300		

TABLE II. - MINIMUM IGNITION DELAY DATA FROM WIRE IGNITION



FIGURE 5. Variation of ignition delay with Halon concentration for ignitions of stoichiometric n-pentane-air mixtures (1 atm) and various Halons with a platinum wire (0.016-inch diameter by 1-1/4-inch long) at 2070°F.



FIGURE 6. Effect of initial wire temperature on the ignition delay of stoichiometric n-pentane-air mixtures (1 atm) with 0.5 volume percent Halon 1301.



FIGURE 7. Effect of fuel concentration on the ignition delay of n-pentane-air mixtures (1 atm) with 0.5 volume percent Halon 1301 (wire temperature - 2150°F).

2. <u>Inhibitor Effectiveness in Exploding Wire and Incendiary</u> <u>Ignitions</u>

Since the ignition delays of flammable mixtures can be negligible and vary little with inhibitor concentration if the ignition energy is excessive, no ignition delay data were obtained in the exploding wire and incendiary ignition experiments. Another difference between the heated wire and the sources used held is that the latter provided multiple ignition sites. With the more effective ignition sources, the inhibitor concentrations required to quench hydrocarbon-air flames were greater than those found with the heated wire source. Table III and Figure 8 summarize the pressure rise data that were obtained in the experiments with stoichiometric n-pentane-air mixtures and the Halon inhibitors at 1 atmosphere pressure using the Pyrofuze wire (0.005 inch diameter by 1-1/4 inches long). With no inhibitor present, the initial rates of pressure rise in the 76 in³ test vessel were close to 600 psi/sec. At the critical inhibitor concentrations required to suppress flame propagation, the corresponding rates were about 150 psi/sec. Also, the maximum pressure rises at the critical conditions were generally less than 5 psi, as compared to over 20 psi when the propagation was not quenched and the explosion relief diaphragm was ruptured. According to these data, Halons 2402 and 1202 ranked about the same in their flame inhibition effectiveness and were slightly more effective on a volume basis than Halons 1301 and 1211. The minimum concentrations for preventing propagation throughout the test mixtures were about 4 to 5 percent for the more effective inhibitors and over 6 percent for the less effective ones. The least effective inhibitor in these experiments was Halon 1011, although the data for this high boiling point material (Table I) were not complete.

Pressure rise data from experiments with the incendiary powder (0.17 gm) as the ignition source are summarized in Table IV and Figure 9. The effect of Halon concentration on the initial rate of pressure rise (Figure 9) appears to be similar to that observed in the experiments with the Pyrofuze wire. However, the results with the incendiary source were less reproducible with each of the Halons used primarily because the energy distribution and the rate of release can vary greatly with such an extensive source. In any case, the critical inhibitor concentrations for quenching the n-pentane-air ignitions with the various Halons were between 5 and 8 percent (see Table IV) and comparable to those required using the Pyrofuze ignition source. Based on the maximum pressure rises developed, Halons 2402 and 1202 displayed the greatest inhibiting effect. Except for Halon 1301, the initial rates of pressure rise at a given inhibitor concentration tended to be lower than those obtained in the exploding wire ignitions (Figure 8); poor initiation of the incendiary powder could partly account for the low rates.

TABLE III. PRESSURE RISE DATA FROM EXPLODING WIRE IGNITION EXPERIMENTS WITH VARIOUS HALONS (2402, 1202, 1301, 1211 and 1011) AND STOICHIOMETRIC n-PENTANE-AIR MIXTURES AT 1 ATMOSPHERE PRESSURE. Pyrofuze Wire - .005 inch diam. by

1-1/4 inches long

Added	Pressur	e Rise, ¹ /	
Halon, Vol.%	(dp/dt) _{initial} psi/sec	△P _{max} 2/ psi	Flame Propagation
		Halon 1011	
0	590 ± 70	>20	Yes
2	370 ± 5	>20	11
3	360 ± 5	>20	11
-		Halon 2402	
0	590 ± 70	>20	Yes
2.0	325 ± 50	>20	**
3.5	175 ± 20	>20	**
5.0	150 ± 40	1.9	No
7.5	125 ± 45	1.1	**
		Halon 1202	
0	590 ± 70	>20	Yes
4.0	155 ± 25	>20	**
6.0	125 ± 5	2.7	No
8.0	110 ± 20	2.4	
		Halon 1301	
0	590 ± 70	>20	Yes
2.0	330 ± 10	>20	"
6.0	175 ± 15	>20	**
8.0	125 ± 50	2.5	No
10.0	140 ± 5	1.1	11
		Halon 1211	
0	590 ± 70	>20	Yes
4.0	235 ± 85	>20	11
6.0	170 ± 25	>20	
8.0	130 ± 15	3.5	No
10.0	105 ± 10	2.0	

1/ Average values for 3 to 4 runs.

2/ Pressure required to rupture explosion relief diaphragm of the test vessel was approximately 20 psig.

TABLE IV. PRESSURE RISE DATA FROM INCENDIARY IGNITION EXPERIMENTS WITH VARIOUS HALONS (2402, 1202, 1301 and 1211) AND STOICHIOMETRIC n-PENTANE-AIR MIXTURES AT ATMOSPHERIC PRESSURE.

T, Added Pressure Rise (dp/dt) initial ΔP_{max}^{27} Halon, Flame Vol.% psi/sec Propagation psi Halon 2402 0 625 ± 60 >20 Yes 1.7 155 ± 50 >20 ... 11 >20 3.3 50 ± 5 5.0 40 ± 5 No 1.0 Halon 1202 625 ± 60 >20 Yes 0 ** 3.3 >20 80 ± 40 5.3 35 ± 5 7.0 No Halon 1301 625 ± 60 0 >20 Yes .. 540 ± 80 1.0 >20 ... 1.8 350 ± 80 >20 ** 6.0 210 ± 35 >20 7.0 130 ± 20 8.0 No Halon 1211 0 625 ± 60 >20 Yes ... 65 ± 10 >20 3.7 .. 35 ± 5 >20 5.5 7.7 - -<1 No

Incendiary Composition (IM-11) - 0.17 gm

1/ Average values for 2 to 8 runs

2/ Pressure required to rupture explosion relief diaphragm of the test vessel was approximately 20 psig.



FIGURE 8. Variation of initial rate of pressure rise with Halon concentration for ignitions of stoichiometric n-pentane-air mixtures (1 atm) and various Halons with a Pyrofuze wire (0.005-inch diameter by 1-1/4-inch long).



FIGURE 9. Variation of initial rate of pressure rise with Halon concentration for ignitions of stoichiometric n-pentaneair mixtures (1 atm) and various Halons with an incendiary powder (0.17 gm).

Figure 10 compares the variation of initial rates of pressure rise with inhibitor concentration for ignitions of stoichiometric n-pentaneair mixtures and Halon 1301 with the incendiary powder, Pyrofuze wire, and Chromel C fuse wire. From this figure it is evident that inhibitor effectiveness is strongly dependent upon the strength of the ignition source. These data indicate that the rates of pressure rise (average values for 4 to 6 runs) for mixtures containing this inhibitor are noticeably lower in ignitions with the Chromel C wire than tiwh the incendiary powder or Pyrofuze wire. As noted, the initial rates of pressure rise with the Chromel C wire ignition source decreased from 560 psi/ sec without any inhibitor to 60 psi/sec with 1.8 percent Halon present. They decreased only slightly with a further increase in Halon concentration and were less than 30 psi/sec at 8 percent Halon, where flame propagation was fully quenched using all three ignition sources. Here, it also appears that the dependence of the pressure rise rates on inhibitor concentration is slightly less with the incendiary ignition source than with the Pyrofuze wire. This is expected since the incendiary source had a greater mass and provided a greater amount of thermal energy for ignition.

The effect of total mixture pressure on inhibitor effectiveness was investigated in exploding wire (Pyrofuze) experiments with Halon 1301 and n-pentane-air mixtures at pressures from 5 to 20 psia. Figure 11 shows a plot of the initial rates of pressure rise vs total mixture pressure obtained with test mixtures containing Halon concentrations of 4, 6 and 8 volume percent. As expected, the rates decreased with decreasing pressure and increasing inhibitor content. The mixtures with 4 percent Halon propagated flame over the range of test pressures but the 6 percent mixtures, which were borderline in flammability at 15 psia, could not be ignited at 5 psia. The mixtures with 8 percent Halon also could not be ignited at the 5 psia test pressure.

B. Fire Suppression Techniques for Aerospace Vehicles

1. Characterization of Burning in Fire Extinguishing Experiments

Initially, the combustibles were burned in air on vertical racks in the 216 ft³ chamber without extinguishing the fires. Following ignition of a combustible, the burning spread upward slowly for a few seconds or more, depending upon the combustible and loading, and then accelerated to a maximum rate until most of the combustible was consumed. The pressures produced during most of the burning period varied as a simple exponential function of time. Figure 12 shows a log-log plot of the pressure rise and time obtained from a least squares fit of replicate test data for cotton and paper sheeting burned on single and double racks; the loading in all runs was 0.035 oz/ft^3 . These data are represented by the following expressions,



FIGURE 10. Variation of initial rate of pressure rise with Halon 1301 concentration for ignitions of stoichiometric n-pentaneair mixtures (1 atm) with an incendiary powder, Pyrofuze wire, and Chromel fuse wire.



FIGURE 11. Effect of total pressure on the initial rate of pressure rise in exploding wire ignitions with stoichiometric n-pentane-air mixtures containing 4, 6, and 8 percent Halon 1301; (0.005-inch diameter by 1-1/4-inch long Pyrofuze wire).



FIGURE 12. Pressure rise versus time for the burning of paper and cotton sheeting (0.035 cz/ft³) in air on single and double burning racks in a 216 ft³ chamber (1 atm).

Cotton Sheeting (1 rack),	6 < t < 32 seconds	
$\ln \triangle P = 2.712 \ln t - 7.306$	s = 0.127	(1)
Cotton Sheeting (2 racks),	l < t < l3 seconds	
$\ln \triangle P = 2.054 \ln t - 3.238$	s = 0.054	(2)
Paper Sheeting (1 rack),	1 < t < 10 seconds	
ln △P = 1.981 ln t - 2.278	s = 0.036	(3)
Paper Sheeting (2 racks),	l < t < 8 seconds	
ln △P = 2.101 ln t - 2.156	s = 0.073	(4)

where $\triangle P$ is the pressure rise in psi, t is the time in seconds, and s is the standard deviation. As expected, the paper combustible burned at the higher rates and produced the higher rates of pressure rise. With a single burning rack, the average rates of pressure rise generally were slightly over 1 psi/sec for the paper sheeting and not more than about 0.5 psi/sec for the cotton sheeting. The corresponding average rates with a double rack at the same loading (0.035 oz/ft³) tended to be at least about 1-1/2 times greater than with the single rack; the effect of the increased surface area was greatest for the slower burning material (cotton).

The pressure rise data provided a reasonably good approximation of the combustible consumed during an experiment. Figures 13 and 14 compare the variation of peak pressure rise and weight loss of combustible with preburn time obtained in extinguishing cotton, paper, and nylon (65%)paper (35%) sheeting fires with 6 percent Halon 1301. Combustible loading was 0.035 oz/ft³ and the Halon was discharged at 350 psig from the Walter Kidde bottle (378 in³) equipped with a 1-1/2-inch diameter pipe nozzle. In each of these figures, the curves indicating the percent weight loss of combustible are very similar to those describing the peak pressure development in the chamber. According to these data, a double and single rack (36 inch by 27 inch) of cotton sheeting is totally consumed within about 15 and 35 seconds, respectively, as compared to corresponding values of 10 and 15 seconds for the paper sheeting on 36 by 42inch racks. Also, the nylon-paper combination appeared to burn about as rapidly as the cotton combustible. The average consumption rates during the period of intense burning were as follows:

> Cotton Sheeting (1 rack); Rate = 0.38 oz/sec " (2 racks); Rate = 0.77 oz/sec Paper Sheeting (1 rack); Rate = 0.94 oz/sec " (2 racks); Rate = 1.17 oz/sec Nylon(65%)-Paper(35%) Sheeting (1 rack); Rate = 0.35 oz/sec



FYCURE 13. Peak pressure rise and weight loss of combustible versus preburn time in extinguishing cotton sheeting fires with 6 percent Halon 1301 in air at a combustible loading of 0.035 oz/ft³. (Pipe nozzle, 350 psig discharge pressure).



FIGURE 14. Peak pressure rise and weight loss of combustible versus preburn time in extinguishing paper and nylon (65 percent)-paper (35 percent) sheeting fires with 6 percent Halon 1301 in air at a combustible loading of 0.035 or/ft³. (Pipe nozzle, 350 psig discharge pressure).

In previous experiments, $\frac{3}{4}$ a 3-volume percent concentration of Halon 1301 was borderline in extinguishing cotton sheeting fires by the total flooding mode. Since 6 percent of the agent in the 216 ft³ chamber proved to be adequate, this Halon concentration was used in most of the present work to evaluate agent effectiveness and toxic product formation in extinguishing cotton, paper, and paper-nylon sheeting fires under various combustible loading and agent discharge conditions. Table V summarizes the extinguishing times from total flooding experiments in which the agent was discharged at 350 psig from extinguisher bottles equipped with an open pipe nozzle, a shower manifold, and a dispersion nozzle; data are also included on the amount of combustible and oxygen consumed. With the pipe nozzle discharge mode, most extinguishing times were equal to or less than 2 seconds and tended to be slightly higher for cotton sheeting than for the other two combustibles at equivalent loadings and preburn times. The longer extinguishing times for the cotton sheeting are partly attributed to the porous nature of this combustible; also, although the paper sheeting produced the largest fires, this material was easily torn by the wind from the Halon discharge, making it less difficult to extinguish the burning between layers. Generally, the extinguishing times with the pipe nozzle were shorter than with a dispersion nozzle (both were directed against the chamber walls) but longer than with a shower manifold which discharged directly onto the burning specimen. The data in Table V also show that the oxygen consumption correlated with the combustible consumption but was not great under the various loadings.

2. Toxic Product Formation With Halon 1301

Gas samples were taken at various preburn times since the toxic product formation of extinguishants is dependent upon such variables as the size of the flame and area of the burning surface at the time of extinguishment. The duration of contact of the extinguishant with the flame is also important. Figures 15 to 17 compare the variation in hydrogen fluoride (HF) and hydrogen bromide (HBr) with preburn time obtained in extinguishing cotton, paper, and nylon (65 percent)-paper (35 percent) sheeting fires on single and double racks in the 216 ft³ chamber; the combustible loading was 0.035 oz/ft^3 and the Halon discharge pressure was 350 psig. Data for both 30 and 240-second samples after extinguishment are plotted in these figures; inaccuracies due to incomplete mixing should be greater for the 30-second samples.

In extinguishment of the cotton sheeting fires on a single rack, the HF and HBr concentrations tended to peak at a preburn time of 10 seconds. However, with two racks at the same loading, only the HF concentration peaked at this preburn time; the HBr appeared to be near maximum at the shortest preburn time (5 seconds) used. Higher concentrations of HF than HBr were produced in the extinguishing experiments with all three types of combustible sheeting. The highest concentrations of these toxic products were generally obtained with the paper sheeting at most

(<u>35 PERC</u> pustible bading, Burni pz/ft ³ Rack	ENT) SHEFT	ING IN A 216	FT J TEST CH	AMBER: (HALON D	DISCHARGE PRESSI	URE - 350 PSIG).
oustible Dading, Burni Dz/ft ³ Rack						
vustible Burni sz/ft ³ Rack						
ading, Burni 2z/ft ³ Rack	Extin	nguisher	Preburn	Combustible	0xygen <u>4</u> /	Extinguishing
)z/ft ³ Rack	ng Dist	charge	Time, .	Consumed	Difference	Time,
	S M	ode	sec.	WC.2	Vol.7	sec.
			Cotton	Sheeting		
0.018 1	Pipe 1	Nozzle	10	33	:	0.4
0.035 1	2		25	85	3.6	0.8
	:		15	13	2.1	1.9
1	2		10	11	2.0	1.0
	:		Ś	4	1.4	1.2
	I		12	80	3.2	1.6
	2		10	77	1.4	4.0
	:		\$	60	1.9	<1.0
0.070 1	:		10	10	1.5	1.8
0.018 1	Shower	r Manifold	10	38	1.9	0.4
0.035 1	:		10	12	:	0.6
0.070 1	:		10	80	1.6	0.3
.018 1	:		10	25	1.9	3.0
0.035 1	Dispei	rsion Nozzle	25	60	2.8	3.5
-	1		15	22	2.2	3.0
	2		10	9	2.0	<1.0
0.070 1	:		10	2	1.6	2.0
	1		Paper	Sheeting		
0.035 1	Pipe 1	Nozzle	80	72	2.6	0.7,
-	:		9	36	1.8	2.0 ⁰ /
	: :		m 1	21	1.5	0.6
			80	95	3.1	0.6
- 7	2		9	74	2.9	0.4
			m .	13	2.7	1.5%
-	n1sbei	atzzou uotsi	0 Nulon-Ben	DO Chanting	8	4.0
0.035 1	Pipel	lozzle		53	8	7 0
	-		10	24	2.5	0.5
-	:		S	5	1.3	0.2
0.070 2	2		10	19	1.6	0.8



FIGURE 15. Hydrogen bromide and hydrogen fluoride concentrations (2 sampling times) versus preburn time in extinguishing cotton sheeting fires with 6 percent Halon 1301 in air at a combustible loading of 0.035 oz/ft³. (Pipe nozzle, 350 psig discharge pressure).



FIGURE 16. Hydrogen bromide and hydrogen fluoride concentrations (2 sampling times) versus preburn time in extinguishing paper sheeting fires with 6 percent Halon 1301 in air at a combustible loading of 0.035 oz/ft³. (Pipe nozzle, 350 psig discharge pressure).



FIGURE 17. Hydrogen bromide and hydrogen fluoride concentrations (2 sampling times) versus preburn time in extinguishing nylon (65 percent)-paper (35 percent) sheeting fires with Halon 1301 in air at a combustible loading of 0.035 oz/ft³. (Pipe nozzle, 350 psig discharge pressure).

preburn times, particularly in the experiments with two burning racks. With an 8-second preburn, approximately 700 ppm of HF and 80 ppm of HBr were detected in extinguishing the fires with this rapid burning material; these values may be compared to a maximum of about 200 ppm of HF and 30 ppm of HBr that were detected in the cotton sheeting fires with a 10-second preburn. The results for the nylon-paper combination were comparable to those for the cotton sheeting, except for the high HBr value (240 sec sample) observed at a preburn time of 17 seconds. At this late burning stage, the nylon-paper fires begin to resemble more closely those of paper than of cotton.

The carbon monoxide (CO) formation, which results from both combustion and extinguishment, was also determined in the above experiments. As expected, the CO increased with an increase in the preburn time or amount of combustible consumed and was greater for the more rapidly burning materials. Figure 18 summarizes the CO variation with preburn time for the Halon 1301 (6 percent) extinguishing experiments with each combustible. The highest CO concentrations (2000-4000 ppm) were formed in the paper and cotton sheeting fires where the effect of the increased surface area from the use of multiple burning racks was also evident. With the nylon-paper sheeting, the CO was less than 500 ppm. Although the concentrations of CO, HF, and HBr were not as high as their lethal concentrations for short exposure times, they would not be safe for exposure times much greater than 15 minutes. Even at HF and HBr concentrations slightly above their threshold limit values (Table VI), brief exposures can be expected to produce some ill effects, including irritation to the eyes, nose and lungs. Furthermore, the use of higher Halon 1301 concentrations than 6 percent can result in higher toxic decomposition product concentrations than described above. For example, the HF concentration increased from 60 to 122 ppm and the HBr from 3 to 37 ppm when the Halon content was increased to 10 percent in extinguishing the cotton sheeting fires after a 25-second preburn time; the loading was 0.035 oz/ft³ on a single rack.

	Threshold Limit Value, ^{a/} ppm	Approximate Lethal Concentration, ppm
Hydrogen fluoride	3	2.500 ^b /
Hydrogen bromide	3	4,750 ^b /
Bromine	-	550 ⁰ /,
Carbon monoxide	50	15,0005/

TABLE VI.	-	TOXIC	LIMITS (OF	PRODUCT	GASES	OR	VAPORS.

<u>a</u>/ Threshold Limit Values for 1968, American Conference of Governmental Hygienists.

b/ National Fire Protection Assn., Standard on Halogenated Fire Extinguishing Agent Systems, NFPA No. 12A-1971.

<u>c</u>/ Freon FE 1301 Fire Extinguishing Agent, DuPont Bull. B-29B, 1969.





The toxic decomposition products of Halon 1301 also varied with the combustible loading and the extinguisher discharge mode. A comparison of such data is shown in Figure 19 from experiments with cotton sheeting fires that were extinguished after a preburn time of 10 seconds using three agent discharge modes. As noted, the HBr and HF concentrations in these runs peaked at a combustible loading of 0.035 oz/ft³ and were highest when the dispersion nozzle was used. These results are not altogether surprising since the longest extinguishing times usually resulted in the runs with the dispersion nozzle (Table V). Also, since only one rack was used with four layers of cotton sheeting at the 0.07 oz/ft³ loading, the size of the fire and the toxic product concentration would not necessarily increase as a result of increasing the loading from 0.035 to 0.07 oz/ft³.

3. Toxic Product Formation With Halon 38

The toxicity hazard of Halon 38 was investigated only in small-scale experiments in the 12 ft³ chamber with cotton sheeting fires at loadings of 0.035 or 0.07 oz/ft³. Results from most of these experiments are summarized in Table VII. With premixed mixtures of the Halon and air, a 6 percent concentration was not adequate for extinguishment but a 12 percent concentration appeared sufficient even though incandescent burning was observed for relatively long periods (>10 seconds). In the total flooding experiments, the 12 percent Halon concentration proved adequate at combustible loadings of 0.035 and 0.07 oz/ft^3 ; at the 0.035 oz/ft^3 loading and various preburn times, the extinguishing times were less than 1 second. However, the HF concentrations at the 0.035 oz/ft³ loading and 20-second preburn time were over 1000 ppm. Compared to the results previously obtained $Z^{1/2}$ for Halon 1301 under similar test conditions, the Halon 38 is less effective and produces higher HF concentrations in the extinguishment of such Class A fires. On the other hand, this perfluorohydrocarbon does not form the more highly toxic HBr or Br, vapors which are possible with Halon 1301.

CONCLUSIONS

The flame inhibition effectiveness of the five Halon materials increases greatly with an increase in inhibitor concentration and with a decrease in the temperature or energy of the ignition source. Ignition delays from heated wire ignitions at 2070°F with n-pentane-air-Halon mixtures indicated that the order of inhibitor effectiveness decreased as follows:

Halon 2402 > Halon 1202, Halon 1301, Halon 1211 > Halon 1011.

All of the Halons are much more effective explosion suppressants than nitrogen. However, with a high energy source such as an exploding wire or incendiary composition, they have little effect on the ignition delay of stoichiometric n-pentane-air mixtures, although the rates of pressure

7/ Work cited in footnote 3.



FIGURE 19. - Hydrogen bromide and hydrogen fluoride concentrations versus combustible loading in extinguishing cotton sheeting fires with 6 percent Halon 1301 by various discharge modes. (350 psig discharge pressure).

S	bustible	Halon	Preburn	Material		Extinguishing		Gas Analy	sis
	.oading,	8	Time,	Consumed,	△Pmax.	Time,	HP,	mqq	CO, ppm
	02/ft ²	Vol.7	sec	Wc.2	psi	sec	5 sec	240 sec	240 sec
					: ;		(
		X	cinguishmer	TOT MICH TOT	al Floodin	ig Mode (Injecti	on Pressu	re 220 psig)	
	0.035	9	20	11	4.3	61	166	142	1000
	:	10	20	59	4.0	2	337	545	6 0U
	:	12	S	S	2.0	7	353	296	007
	2	12	10	18	2.1	⊽	552	223	300
	:	12	20	11	4.9	7∨	1444	1472	300
	:	12	20	57	4.0	₽	1794	1209	800
	0.070	12	20	13	2.3	1.4	123	156	400
			Exting	puishment W	lith Premix	ed C3F8-Air Mix	tures		
	0.035	9	0	92	5.0	33	1715	:	1000
	:	12	0	9	0.2	13ª/	458	865	1000
ेला	Largely	incandes	c ent type b	urning.					

 TABLE VII.
 DATA FROM FIRE EXTINGUISHING EXPERIMENTS WITH PERFLUOROPROPANE (HALON 38)

 AND COTTON SHEETING IN A 12 FT³ CYLINDRICAL CHAMBER.

37

rise are reduced with the addition of these Halons (≤ 10 volume percent). According to the pressure rise data, Halons 2402 and 1202 were slightly more effective than Halons 1301 and 1211 in suppressing the ignitions initiated with these high energy sources; the effective Halon concentrations were between 4 and 8 percent.

Cotton sheeting, paper sheeting, and nylon-paper sheeting fires can be rapidly extinguished with 6 volume percent Halon 1301 when the agent is dispersed by the total flooding mode and the combustibles are vertically mounted. The extinguishing times tended to be slightly higher with the cotton sheeting than with either the nylon (65 percent)-paper (35 percent) sheeting or the paper sheeting, which gave the highest burning rates and pressure rise rates at various combustible loadings $(\leq 0.07 \text{ oz/ft}^3)$ in a 216 ft³ chamber. The toxic product formation varied particularly with preburn time, combustible loading, combustible composition, and the agent discharge mode. Highest HBr and HF concentrations occurred in the paper sheeting fires, although the concentrations were not as high as the lethal values reported for short exposure times. Also, the extinguishing times and toxic product formation were greater with the use of a dispersion extinguisher nozzle than with a pipe nozzle or shower manifold discharge mode. In addition, small-scale experiments with Halon 38 indicate that this agent produces higher HF concentrations than Halon 1301 in extinguishing cotton sheeting fires, primarily because of the higher Halon 38 concentrations required.

RECOMMENDATIONS

In order to evaluate other materials and techniques for suppressing fires and explosions, including those under gun firing conditions, the following recommendations are made for future work:

(1) Determine effectiveness of halogerated flame inhibitors to suppress ignitions in aircraft fuel tanks under simulated incendiary gun firings. Investigate other classes of flame inhibitors which may be useful for reducing internal ignition hazard or external fire hazard when fuel tanks are subjected to gun firings.

(2) Compare performance of Halon 38 with that of Halon 1301 in largescale fire extinguishing experiments with Class A fires. Investigate other promising extinguishants including perfluorobutane, pentafluorobromoethane, and trifluoroiodomethane.