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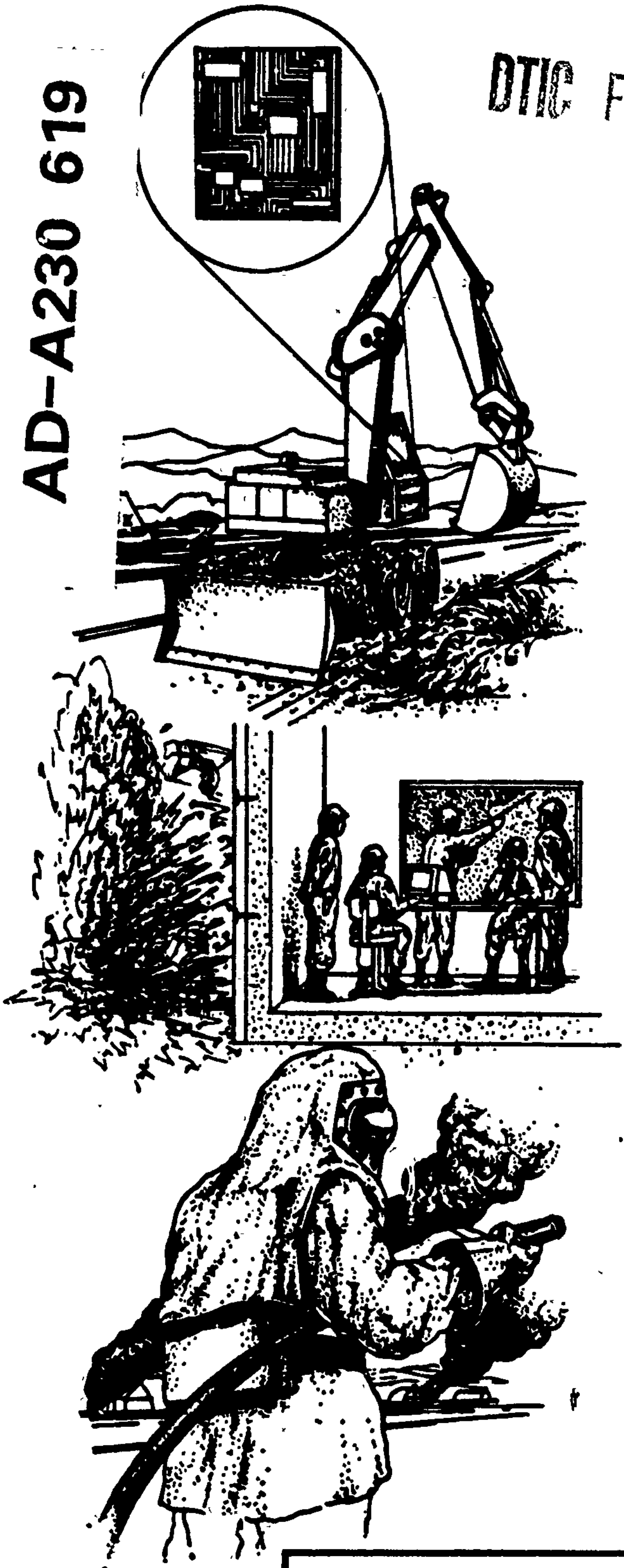

NEXT-GENERATION FIRE EXTINGUISHING AGENT PHASE III

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This project was established to originate concepts for next-generation fire extinguishing agents. In Phase III, an effort to develop a substitute agent to replace Halon 1211 in Air Force firefighter training was initiated. Laboratory-scale investigations of flame extinguishment by chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCSCs) were performed. Laboratory studies of physical properties of CFC blends were also carried out.

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EXECUTIVE SUMMARY

A. OBJECTIVE

The objective of the overall effort is to originate concepts for a next-generation suppressant for multidimensional fires. The objective of this Phase III effort was to initiate an effort for the development of an agent to substitute for Halon 1211 in Air Force firefighter training.

B. BACKGROUND

Although many new types of fire suppressants have been originated, improved agents are still needed. Halons, for example, are highly effective against flowing liquid fuel fires and indirectly accessible aircraft engine fires. However, they give poor security and have poor diliverability, particularly outdoors with adverse winds. Some halons also have significant toxicity problems and potentially unacceptable environmental impacts, particularly depletion of stratospheric ozone.

In Phase I, a study of flame suppression and fire extinguishment concepts was performed, and a recommendation was made that research efforts emphasize halons and halon-like materials having a low potential to deplete stratospheric ozone. In Phase II, testing of halon-like agents that could serve as alternatives to the present halons was initiated. The Phase I analysis of combustion and suppression was reviewed and expanded, and laboratory studies on flame extinguishment and laser Raman spectroscopy were initiated.

C. SCOPE

The scope of the overall project is to originate concepts for new fire extinguishing agents. In Phase III, an effort to develop a substitute agent to replace Halon 1211 in Air Force firefighter training was initiated. Laboratory-scale investigations of flame extinguishment by some chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) were performed. Laboratory studies of physical properties of CFC blends were also carried out.

D. METHODOLOGY

Several experimental methods were used in this phase. Still photography was used to characterize the droplet size and pattern during discharge of halon-like agents. A laboratory-scale discharge apparatus was built and its performance was validated using Halon 1211 and HCFC-22. Small-scale discharge tests on Halon 1211, HCFC-22, and CFCs 11, 12, and 114 were conducted in the Combustion Engineering Laboratory on Kirtland AFB. Two formulations (domestic and advanced) of a mixture called Composite Advanced Halon (CAH) were also tested on a laboratory scale. These mixtures consisted of blends of CFCs 11, 12, 113, and 114, plus a proprietary homogenizing agent. The CAH formulations were tested using aerosol cans to extinguish JP-5 fuel fires in a 6-inch square pan. Cup burner tests were also conducted on both formulations of CAH. A series of tests to investigate the inerting action of domestic formula CAH was performed.

E. TEST DESCRIPTION

A laboratory-scale discharge extinguishment apparatus was designed and constructed during this phase, and several configurations were tested using control agents.

F. RESULTS

In laboratory-scale discharge tests, the flow rates, valve settings, and pressures needed for flame extinguishment by HCFC-22 and by Halons 1211 and 2402 in the test apparatus were determined. In small-scale discharge extinguishment testing, it was shown that CFC-114 and CFC-11 extinguished fires. No extinguishment was obtained with CFC-12 or CFC-22 under the small-scale discharge test conditions.

G. CONCLUSIONS

It was shown that photographic methods can provide an acceptable and cost-effective method for determining and documenting drop-size distributions during discharge of halon-like agents. Sufficient work was performed to demonstrate the usefulness of the laboratory-scale discharge apparatus for characterization of agents delivered by streaming. Small-scale discharge extinguishment tests verified the expectation that, for agents delivered by streaming, extinguishment is highly dependent on boiling point.

H. RECOMMENDATIONS

It is recommended that mixtures of CFCs and/or HCFCs be tested further as potential training agents. The boiling points of these agents should be high enough to offset the inherently lower fire suppression alilities of these materials compared to Halons. A survey of generally available CFCs and HCFCs should be conducted, with particular emphasis on toxicity and environmental characteristics. Extinguishment tests on medium- and large-scale pool fires should be conducted on selected materials.

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PREFACE

This report was prepared by the New Mexico Engineering Research Institute (NMERI), University of New Mexico, Albuquerque, New Mexico 87131, under contract F29601-84-C-0080, for the Engineering and Services Laboratory, Air Force Engineering and Services Center, Tyndall Air Force Base, Florida 32403.

This report summarizes work done between December 1987 and August 1988. The HQ AFESC/RDCF Project Officer was Major E. Thomas Morehouse.

This report has been reviewed by the Public Affairs Officer (PA) and is releasable to the National Technical Information Service (NTIS). At NTIS it will be available to the general public, including foreign nationals.

This technical report has been reviewed and is approved for publication.

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

SECTION I
INTRODUCTION

A. OBJECTIVE

The objective of the total effort is to originate concepts for a next-generation suppressant for multidimensional fires with a complete analysis of the molecular basis for the agent action and of the quantitative burning inhibition obtained. The objective of the Phase III effort is to initiate an effort for the development of an agent to substitute for Halon 1211 in Air Force firefighter training.

B. BACKGROUND

Although many new types of fire suppressants have been originated, improved agents are still needed. The fires of primary interest in ground-based fire protection for aerospace vehicles are Class B (liquid fuel) fires. Three types of agents are used by the Air Force and Navy for Class B fires (Reference 1). Foams, such as aqueous film-forming foam (AFFF), have low toxicities and provide excellent security against flashback and burnback of liquid fuels; however, foams are not three-dimensional and are dirty. They leave residues which can adversely affect aircraft engines and electronic components. Solid agents, such as potassium bicarbonate ($KHCO_3$), are excellent suppressants against liquid fuel fires (Reference 2); but, they too are dirty, have poor deliverability, and give only moderate security. Halons (Reference 3) have excellent dimensionality (they are highly effective against flowing liquid fuel fires and indirectly accessible aircraft engine fires), and they are clean; however, they give poor security and have poor deliverability, particularly outdoors with adverse winds. Moreover, some halons have significant toxicity problems and potentially unacceptable environmental impacts. A particularly serious environmental problem is the suspected impact of present-day halon agents (Halons 1211 and 1301) on stratospheric ozone.

In Phase I, a study of flame suppression and fire extinguishment concepts was performed (Reference 4). Toward the end of the Phase I study, the possibility that halon firefighting agents, like chlorofluorocarbons (CFCs), were depleting stratospheric ozone became increasingly apparent. Accordingly, a high priority was given to the development of clean fire extinguishants to replace halons.

Phase II initiated development of a program to find chemical alternatives for Halons 1211 and 1301 (Reference 5). The most critical Air Force agent need is a replacement for Halon 1211, which is the clean agent used for aircraft fires and in the recently designed fire protection system for the Hardened Aircraft Shelter (HAS). Emphasis, therefore, was placed on Halon 1211 alternatives. Halon 1301 replacements were not, however, totally ignored. The Phase II effort encompassed laboratory-scale flame suppression determinations and spectroscopic studies. The following conclusions were made from the results of Phase II:

1. Removal of species involved in tightly coupled chain-branching reactions should be particularly effective in fire extinguishment. Atomic hydrogen is such a species.

2. Sensitivity gradient calculations can be employed with computer models of combustion and extinguishment to determine critical reaction paths, which can be targeted by new agents.

3. Heat absorption by an agent could play an important role in fire extinguishment, even for those agents whose effect is considered to be primarily chemical.

4. The application of shock waves or other methods to momentarily increase ambient pressure during application of a halon-like agent could increase extinguishment ability.

5. Cup burner test results depend on air flow rate, and this must be taken into account during apparatus design and operation.

6. For streaming agents, physical properties may be as important as chemical properties.

7. CFCs and HCFCs are potentially useful clean fire extinguishment agents.

8. Laboratory-scale testing indicates that the inherent flame suppression ability of some selected materials increases in the order HCFC-22 < CFC-12 < CFC-114 < Halon 1211 ($CBrClF_2$). Since this is precisely the prediction which one would make based on the structure, it may be possible to develop algorithms to predict extinguishment ability.

9. Synergism is a common phenomenon for mixtures of halons and CFCs or HCFCs.

10. Laser Raman spectroscopy is a potentially useful tool for the study interactions between flames and halon-like agents.

The following recommendations were made in Phase II:

1. HCFCs, CFCs, and their blends should be targeted for investigation as alternative clean agents for halon replacement.

2. Emphasis on Halon 1211 alternatives should be continued.

3. Development of methods to collect extinguishment data during discharge should receive high priority in future work.

4. Laser Raman studies should be split out as a separate project.

5. Computerized sensitivity analyses should be considered to determine critical reaction paths.

6. An effort should be initiated to develop an agent to substitute for Halon 1211 in Air Force firefighter training.

7. Work on algorithms to calculate fire extinguishment capability from molecular structure and physical properties should be performed.

On 16 December 1987, just before the initiation of Phase II, an international treaty to limit the production of materials that deplete stratospheric ozone was signed in Montreal, Canada. The Montreal Protocol divides these materials into two categories. Category 1 materials encompass CFC-11, CFC-12, CFC-113, CFC-114, and CFC-115. Starting in 1989, the production of Category 1 materials is restricted to 1986 levels. A reduction by 30 percent from 1986 levels is to be imposed in 1993, and a total reduction by 50 percent is to be implemented in 1998.

Category 2 encompasses Halon 1211, Halon 1301, and Halon 2402. The restrictions on Category 2 materials are, at present, less strict than those for Category 1 compounds. Starting in 1992, halon production is to be frozen at 1986 levels.

During Phase II it became increasingly apparent that regulations on Halons 1211 and 1301 would be more strict than those imposed by the Montreal Protocol. It also became apparent that firefighter training caused a large percentage (more than 70 percent) of the Air Force emissions of Halon 1211. A decision was then made to investigate the development of an alternative agent to replace Halon 1211 in training. The feasibility of the early development of a training agent was based on the following rationale.

1. A temporary training agent does not need an Ozone Depletion Potential (ODP) as low as that required for permanent halon replacements. This is not to say that a training agent must be temporary. However, such a decision could be made, depending on the attainable ODP.

2. A training agent needs to mimic the action of Halon 1211 only in one specific scenario: firefighter training with a pool fire containing JP-4 fuel.

3. Since firefighters are professionals and are trained outdoors, toxicity requirements are not as stringent as for a general-purpose agent.

4. Cleanliness and compatibility with advanced airframe materials is not important for an agent to be used solely in firefighter training.

5. A decreased agent effectiveness is not a critical drawback since this may serve to give firefighters better training.

6. Since a decreased agent effectiveness and a slightly higher toxicity level could be acceptable for a training agent, off-the-shelf materials may be available. This availability would greatly reduce the research work needed to develop a product.

The Phase II results indicated that blends of CFCs and/or HCFCs could be used to develop an agent having a decreased ODP to replace Halon 1211 in firefighter training only. Since training accounts for the majority of the Air Force halon emissions, the availability of a training agent would reduce the environmental impact of Air Force operations and would increase the availability of Halon 1211 for essential fire protection requirements.

C. SCOPE

The scope of this task involves the origination of concepts for new fire-extinguishing agents. The concepts may involve any combination of inhibitors that act by chemical and/or physical mechanisms or by new modes of utilization. Hypotheses are tested using laboratory-scale experiments. Fire parameters are monitored throughout the testing to provide information concerning mechanisms of action and to permit feedback for refinement of original concepts and origination of new concepts. Sufficient research to determine the molecular mechanisms of extinguishment of selected agents is also performed. The next-generation agent(s) should be able to suppress one-, two-, or three-dimensional fires with minimal application under a range of ambient conditions. The final product of this project is a technical report detailing all work accomplished, with conclusions and recommendations.

D. TECHNICAL APPROACH

The following tasks are required for Phase III of this project. Candidates for firefighter training agents shall be identified and screened in laboratory-scale and and small-scale Class B fire tests. As needed, additional laboratory testing for characterization shall be performed. To the extent possible, known materials for which significant toxicity and environmental impact data are available shall be used. As needed preliminary field studies may be performed on selected candidates to aid in preparing a Phase IV test plan.

Since this program targets replacement of Halon 1211, an agent delivered by streaming, testing under discharge conditions is an essential part of the alternative agent development. Nearly all laboratory testing of fire extinguishment agents is now performed under nondischarge conditions. No laboratory-scale fire extinguishment discharge test apparatuses have been reported. Accordingly, the examination of methods for laboratory-scale and small-scale evaluations of agent discharge and of fire extinguishment capability for delivery by discharge is given high priority in the present phase.

In the early stages of development of a training agent, consideration is being given to the use of CFC and HCFCs, either as pure agents or as blends. Laboratory testing has demonstrated that these materials are acceptable candidates for testing as replacement agents. Their extinguishment ability may result largely from scavenging of hydrogen atoms, in a mechanism similar to that of the halons. Because of their heat-absorbing capability during vaporization and because of their better streaming properties, higher molecular weight materials, with increased boiling points, could be particularly effective.

In spite of the restrictions on production of CFCs, their use to replace Halon 1211 in firefighter training would decrease the environmental impact of Air Force operations. A commercially available CFC mixture was obtained and laboratory studies on this mixture were performed.

SECTION II
DROPLET SIZING EXPERIMENTS

Since discharge characteristics are very important for a Halon 1211 replacement, some initial work was performed to scope the use of a photographic technique to characterize droplet size and pattern during discharge of halon-like agents. Two tests were conducted to photograph the droplet size of Halon 1301 and Halon 1211 flowing from a nozzle. For each test, a 1-liter stainless steel cylinder was filled with 500 milliliters of agent. Both the Halon 1301 and Halon 1211 tests were run at 70 ^{o}F (294 K) and 200 lb/in.^{2} (1379 kPa). The vapor pressure of Halon 1301 is 200 lb/in.^{2} at this temperature. The Halon 1211 was pressurized to 200 lb/in.^{2} with nitrogen. The valve on the stainless steel cylinder was used as the nozzle.

A 35-millimeter still-frame camera was set on a tripod. The shutter speed was set at 1/1000 second to freeze the movement of the flowing halon. Both cylinders were tilted downward at approximately 30 degrees from horizontal to allow only liquid to flow from the nozzle. In the first series of tests, the valve was opened slightly to allow a very small stream of halon to pass. The first experiments recorded the first 6 inches of the halon stream. These photographs showed droplets ranging in size from 1 millimeter down to an estimated 10 micrometers. The larger droplets could be seen individually; the smaller droplets were, for the most part, indistinguishable and formed a cloud.

The larger Halon 1211 droplets were 1 millimeter in diameter. The smaller droplets could be seen individually. Some of the larger droplets began to fall away from the stream at 2 inches from the nozzle.

In a second series of tests, the valve was opened completely. Once again, the camera was set to show the first 6 inches of the halon streams. Individual droplets were not observed with Halon 1301 under these conditions. The vaporous stream was uniform. The Halon 1211 flow rate was similar to that of the Halon 1301; however, much of the Halon 1211 stream existed as individual droplets having a diameter of approximately 1 millimeter. Even at this higher flow rate, the larger Halon 1211 droplets began falling from the main stream 2 inches from the nozzle, as was seen for the lower flow rate.

A third series of tests was conducted with the camera set 3 feet from the nozzle to show the end of the stream. The Halon 1301 discharge was uniform for the entire stream length. No droplets were observed to fall away from the main body of the flowing vapor. The entire Halon 1301 stream evaporated before touching the ground. Halon 1211, with its higher boiling point, had large droplets falling from the main stream body for the entire length of the discharge plume. At the end of the stream, much of the 1211 remained in large droplets, which evaporated only after remaining on the floor for approximately 10 seconds.

These tests showed that high-speed photography is a viable method for documenting and measuring flow characteristics of halon-like agents.

SECTION III
LABORATORY-SCALE DISCHARGE EXTINGUISHMENT TESTING

A. APPARATUS AND PROCEDURE

Due to the high cost and limited availability of certain materials needed in the evaluation of halon-like agents, a laboratory-scale discharge extinguishment test was needed to evaluate agents for a streaming application. The initial apparatus (Configuration 1) consisted of a 1-liter gas sample cylinder fitted with a gas inlet valve at one end for introducing agents (Figure 1). For agent delivery, an outlet valve, pressure gauge, solenoid, metal tubing, and a small nozzle was placed at the other end. The nozzle tip was located 6 inches from a fuel cup. The solenoid, which was connected to a switch, allowed rapid control of agent delivery. A selection of small nozzles controlled the spray pattern (flat, conical rim, conical full) and the spray angle. The metal tubing permitted adjustment of delivery direction. The apparatus was clamped to a ring stand with the nozzle directed at a metal cup, which was 3 inches high and 3.5 inches in diameter. The cup was surrounded on three sides by fire bricks, which were stacked two high. The entire apparatus was set up in a fume hood.

The preliminary apparatus validation work used Halon 1211 and HCFC 22 to compare apparatus settings to extinguishment flow rates obtained. Halon 1211 was used as a standard due to its excellent extinguishing ability. HCFC 22, which is a much less effective fire suppressant, was used to provide apparatus test data for a relatively poor agent. For all tests, the fuel cup was filled with 100 milliliters of water and 10 milliliters of JP-4 fuel. A stop watch giving times to 0.01 second was used as a timing device. The fume hood fan was operated during all tests.

The first tests were conducted using the following procedure. The tubing and nozzle were detached from the main apparatus and were clamped in the correct position on the ring stand. The cylinder was filled with agent, weighed, attached to the tubing and nozzle, and clamped to the ring stand.

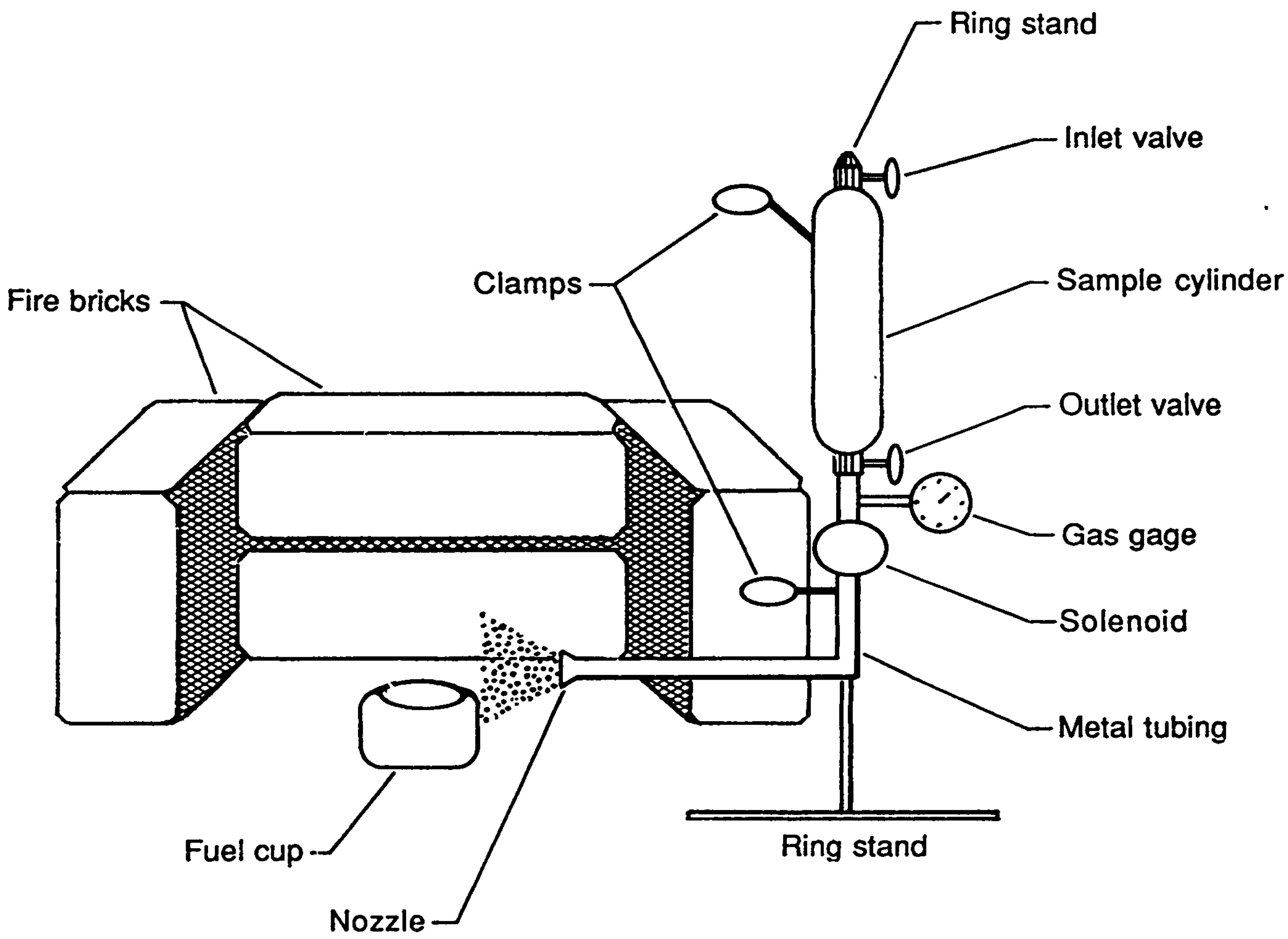

Figure 1. Laboratory-Scale Discharge Fxtinguishment Apparatus, Configuration 1.

The cylinder delivery valve was then opened. The fuel in the metal cup was ignited and allowed to burn for 30 seconds. The solenoid was then activated. At extinguishment, the solenoid switch and stop watch were simultaneously turned off. The main body of the apparatus was detached from the metal delivery tube and weighed. The extinguishment time and weight of agent used were noted, and the flow rate was calculated.

B. RESULTS AND APPARATUS MODIFICATION

All test results are given in Table 1. All tests in the first series used Halon 1211 except for Test Number 7, which used HCFC-22. In that test, the flame was blown out owing to the high vapor pressure of HCFC-22. The first test results revealed three important factors that determined flow rate: the physical state of the agent under ambient conditions, the cylinder pressure, and the nozzle. They also indicated that the test, as configured, might not be sufficiently critical since Halon 1211 extinguished the fire in all cases from discharge rates of 4.40 to 30.44 grams/second.

For a second series of tests, the apparatus was reconfigured as shown in Figure 2. Since the first series of tests showed that better flow control was desirable, a needle valve was added between the solenoid and the nozzle. This decreased the effects of air flow in the fume hood by giving a better-defined agent stream. The series of tests performed (Test Numbers 8 through 16) were for spray pattern checks and flow calculations. No fires were used. The cylinder was pressurized with nitrogen after each test. The tests for the Figure 2 apparatus showed that the needle valve greatly improved flow control.

For the next apparatus configuration (Figure 3), the gas gauge was moved to the inlet side of the cylinder, between the cylinder and the inlet valve. This helped to give more accurate readings when the cylinder was filled and pressurized. Initially the nozzle was aimed at the edge of the cup (Test Numbers 17 through 51). For those tests, Halon 1211 extinguished the fire at flow rates from 4.93 to 20.13 grams/second. Fourteen HCFC-22

TABLE 1. RESULTS OF LABORATORY-SCALE DISCHARGE EXTINGUISHMENT APPARATUS TESTS.

Test No.	Agent	Flow, g/sec	Valve setting	Pressure, $lb/in.^2$	Fire suppression
		Apparatus Configuration 1			
1	Halon 1211	30.44	--	50	Yes
2	Halon 1211	23.49	--	50	Yes
3	Halon 1211	4.62	--	50	Yes
4	Halon 1211	4.40	--	50	Yes
5	Halon 1211	4.62	--	50	Yes
6	Halon 1211	4.40	--	50	Yes
7	HCFC-22	2.82	--	120	Yes
		Apparatus Configuration 2			
8	Halon 1211	2.93	1.0	50.5	--
9	Halon 1211	4.29	2.0	55	--
10	Halon 1211	32.06	3.0	50.5	--
11	Halon 1211	13.25	2.5	40	--
12	Halon 1211	25.40	2.5	60	--
13	Halon 1211	30.42	3.0	62	--
14	Halon 1211	38.20	4.0	50	--
15	Halon 1211	--	2.5	60	--
16	Halon 1211	18.51	2.5	60	--
		Apparatus Configuration 3			
17	Halon 1211	7.67	2.5	60	Yes
18	Halon 1211	12.34	2.5	60	Yes
19	Halon 1211	7.67	2.5	60	Yes
20	Halon 1211	11.31	2.5	60	Yes
21	Halon 1211	14.46	2.5	60	Yes
22	Halon 1211	20.13	2.5	65	Yes
23	Halon 1211	14.50	2.5	60	Yes
24	Halon 1211	15.09	2.5	60	Yes
25	Halon 1211	11.27	2.0	60	Yes

TABLE 1. RESULTS OF LABORATORY-SCALE DISCHARGE EXTINGUISHMENT APPARATUS TESTS (CONTINUED).

Test No.	Agent	Flow, g/sec	Valve setting	Pressure, $lb/in.^2$	Fire suppression
26	Halon 1211	10.10	2.0	60	Yes
27	Halon 1211	15.40	2.0	60	Yes
28	Halon 1211	5.35	1.5	60	Yes
29	Halon 1211	7.79	1.5	65	Yes
30	Halon 1211	3.96	1.5	60	Yes
31	Halon 1211	4.93	1.5	60	Yes
32	Halon 1211	9.59	1.5	60	Yes
33	Halon 1211	12.90	1.5	60	Yes
34	Halon 1211	10.09	1.5	60	Yes
35	Halon 1211	5.48	1.0	60	Yes
36	Halon 1211	5.52	1.0	60	Yes
37	Halon 1211	5.03	1.0	60	Yes
38	HCFC-22	3.66	1.0	138	No
39	HCFC-22	1.39	1.0	138	No
40	HCFC-22	2.43	1.0	145	No
41	HCFC-22	1.91	1.0	150	No
42	HCFC-22	1.31	1.0	133	No
43	HCFC-22	1.35	1.0	139	No
44	HCFC-22	60.34	3.7	132	Yes
45	HCFC-22	13.58	2.5	128	No
46	HCFC-22	10.10	1.5	130	No
47	HCFC-22	7.00	0.75	120	No
48	HCFC-22	5.28	0.75	125	No
49	HCFC-22	6.00	0.75	125	No
50	HCFC-22	4.08	0.75	125	No
51	HCFC-22	23.79	0.75	125	Yes
52	HCFC-22	7.58	0.75	125	Yes
53	HCFC-22	10.55	0.75	118	Yes
54	HCFC-22	9.01	0.75	120	Yes
55	HCFC-22	10.38	0.60	125	Yes
56	HCFC-22	9.65	0.50	125	Yes
57	HCFC-22	7.89	0.40	130	Yes
58	HCFC-22	1.59	0.40	112	No

TABLE 1. RESULTS OF LABORATORY-SCALE DISCHARGE EXTINGUISHMENT APPARATUS TESTS (CONTINUED).

Test No.	Agent	Flow, g/sec	Valve setting	Pressure, $lb/in.^2$	Fire suppression
59	HCFC-22	3.40	0.40	118	No
60	HCFC-22	2.19	0.40	109	No
61	HCFC-22	2.61	0.40	118	Yes
62	HCFC-22	6.90	0.40	118	Yes
63	HCFC-22	3.76	0.40	118	Yes
64	HCFC-22	3.16	0.30	120	No
65	HCFC-22	3.08	0.30	120	No
66	HCFC-22	1.22	0.30	120	No
67	HCFC-22	0.92	0.30	120	No
68	HCFC-22	1.52	0.30	125	No
69	HCFC-22	1.54	0.35	129	No
70	Halon 1211	8.76	0.50	60	Yes
71	Halon 1211	2.41	0.50	60	No
72	Halon 1211	1.74	0.50	60	No
73	Halon 1211	1.31	0.50	60	No
74	Halon 1211	4.00	0.50	60	Yes
75	Halon 1211	2.06	0.50	60	No
76	Halon 1211	1.25	0.40	125	No
77	Halon 1211	1.98	0.50	125	No
		Apparatus Configuration 4			
78	HCFC-22	4.09	1.00	110	Yes
79	HCFC-22	3.62	1.00	120	No
80	HCFC-22	2.36	1.00	111	No
81	HCFC-22	2.62	1.00	115	No
82	HCFC-22	3.12	1.00	115	No
83	HCFC-22	4.73	1.50	120	Yes
84	HCFC-22	4.82	1.70	120	Yes
85	HCFC-22	2.55	1.25	110	No
86	HCFC-22	2.84	1.25	119	No
87	HCFC-22	2.55	1.50	120	No
88	HCFC-22	5.84	1.75	120	Yes

TABLE 1. RESULTS OF LABORATORY-SCALE DISCHARGE EXTINGUISHMENT APPARATUS TESTS (CONCLUDED).

Test No.	Agent	Flow, g/sec	Valve setting	Pressure, $lb/in.^2$	Fire suppression
89	HCFC-22	12.59	1.60	120	Yes
90	HCFC-22	10.77	1.50	125	Yes
91	HCFC-22	8.77	1.50	121	Yes
92	HCFC-22	5.05	1.50	111	Yes
		Apparatus Configuration 5			
93	Halon 1211	2.27	0.70	50	No
94	Halon 1211	7.87	1.00	60	Yes
		Apparatus Configuration 6			
95	Halon 1211	9.50	0.80	60	Yes
96	Halon 1211	11.25	0.70	50	Yes
97	Halon 1211	4.35	0.70	60	Yes
		Apparatus Configuration 5			
98	Halon 1211	12.15	0.70	60	Yes
99	Halon 1211	5.25	0.40	60	No
100	Halon 1211	4.61	0.35	60	No
101	Halon 1211	14.41	0.35	60	Yes
		Apparatus Configuration 7			
102	Halon 2402	37.56	--	85	Yes
103	Halon 2402	65.5	--	90	Yes
104	Halon 2402	62.5	--	100	No
105	Halon 2402	44.6	--	100	No
106	Halon 2402	40.13	--	100	No
107	Halon 2402	28.07	--	100	No
108	Halon 2402	21.49	--	100	No

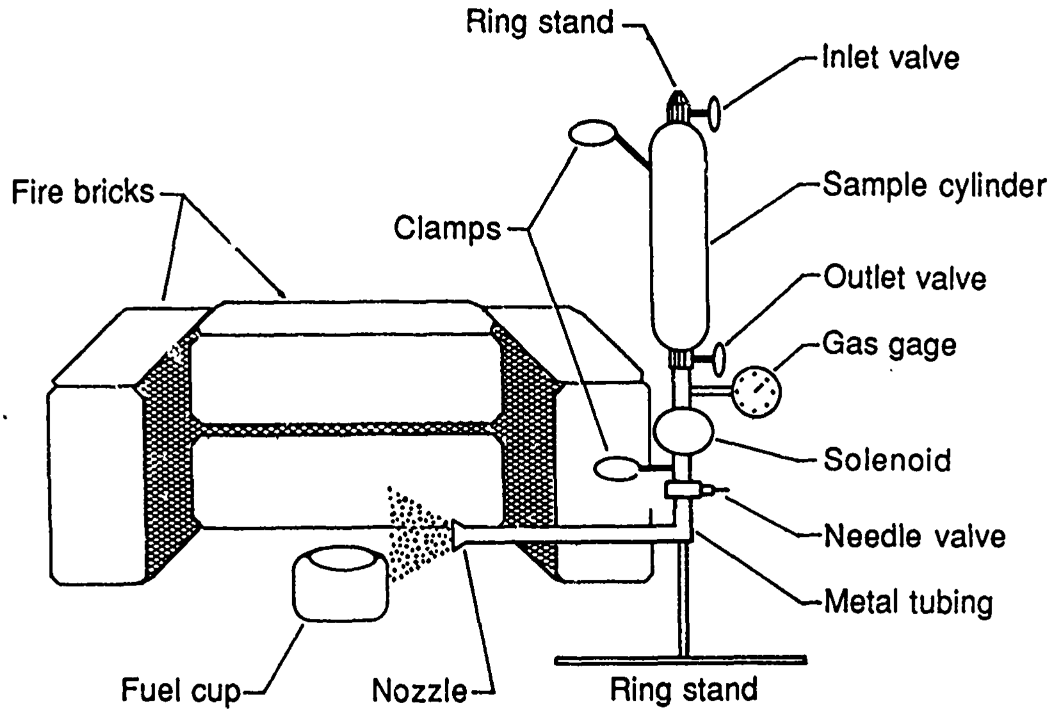

Figure 2. Laboratory-Scale Discharge Extinguishment Apparatus, Configuration 2.

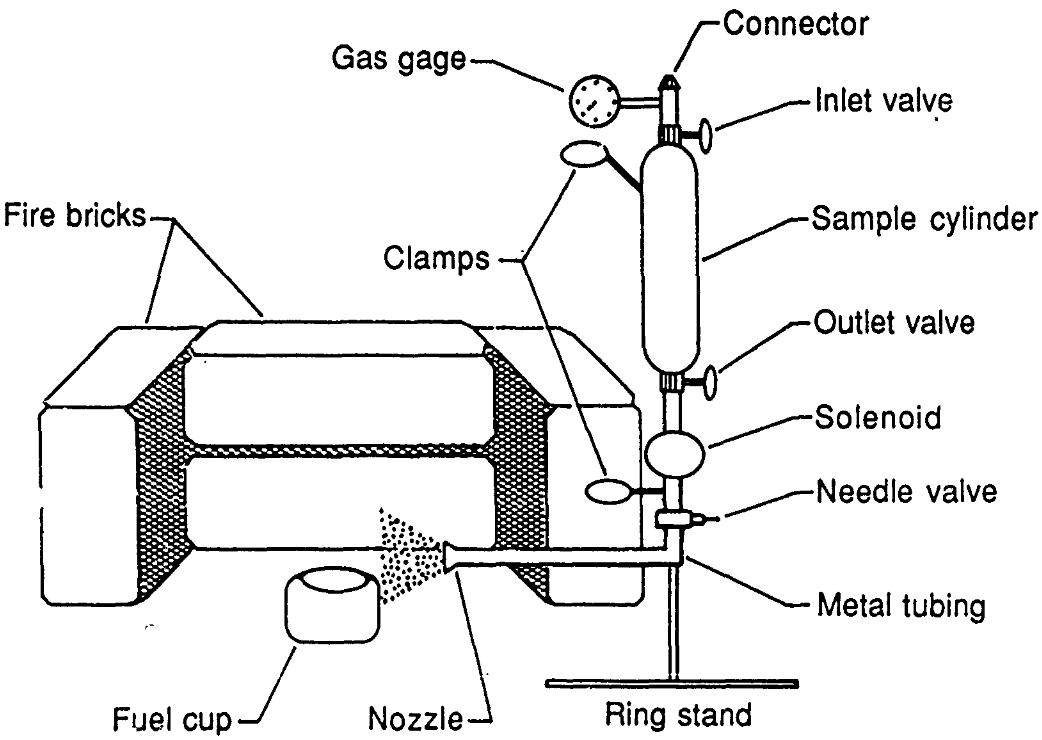

Figure 3. Laboratory-Scale Discharge Extinguishment Apparatus, Configuration 3.

tests were run with this nozzle configuration (flow rates from 1.31 to 60.34 grams/second). Of these, only the two highest flow rates, 23.79 and 60.34 grams/second, extinguished the fire. Extinguishment failed for flow rates of 13.58 grams/second and below.

For Test Numbers 52 through 77, the nozzle was directed to the center of the cup. For this series of tests, the Halon 1211 flow varied from 1.31 to 8.76 grams/second. Two of these test runs extinguished the fire (4.00 and 8.76 grams/second). The remaining six runs (1.31 to 2.06 grams/second) did not. The data for HCFC-22 with this nozzle configuration showed significant overlap. Extinguishment was obtained for HCFC-22 flow rates ranging from 2.61 to 10.55 grams/second. No extinguishment was obtained for flow rates ranging from 0.92 to 3.40 grams/second. Thus in the region of 2.61 to 3.40 grams/second both extinguishment and nonextinguishment were obtained with HCFC-22. These test data showed poorer extinguishment with HCFC-22 than with Halon 1211; however, the difference was not large. This apparatus configuration provided a rigorous test since some flow rates for both Halon 1211 and CFC-22 failed to extinguish the fire.

For Configuration 4, the tubing next to the nozzle was removed to decrease the "dead space" and, therefore, improve the determination of agent flow rate (Figure 4). The needle valve was placed next to the nozzle, and a 2-inch piece of tubing was added between the cylinder and solenoid to allow for more equilibration time. The removal of the end tubing resulted in the placement of the needle valve next to the nozzle and streamlined the apparatus. The nozzle was placed 9.7 inches from the fuel cup. A cradle was made to hold the apparatus at adjustable angles. The cradle was attached to the ring stand and could be adjusted 360 degrees (front to back, side to side). Bricks were placed to surround the cup completely, except for an opening at the side to allow for delivery. This arrangement of fire bricks significantly decreased turbulence from the fume-hood fan.

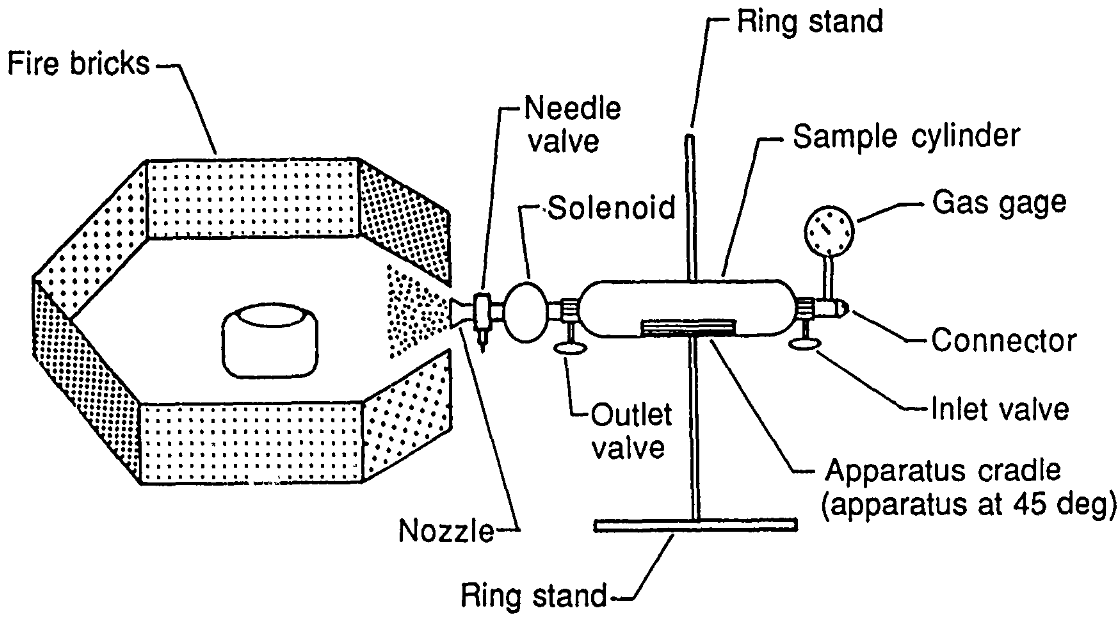

Figure 4. Laboratory-Scale Discharge Extinguishment Apparatus, Configuration 4.

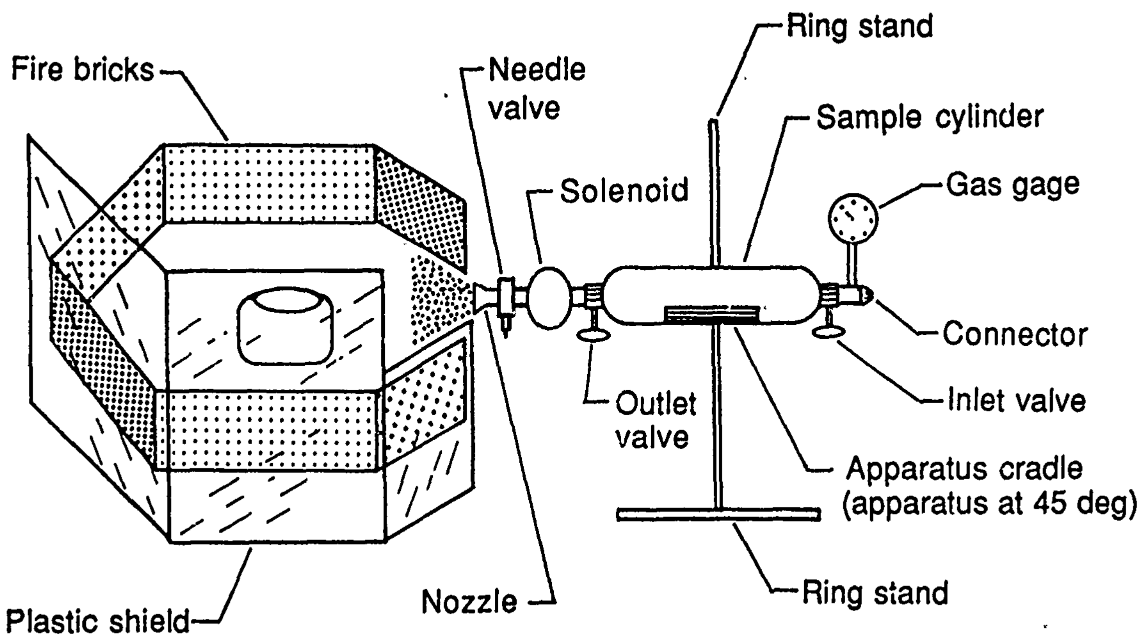

Figure 5. Laboratory-Scale Discharge Extinguishment Apparatus, Configuration 5.

Only HCFC-22 agent was run with Apparatus Configuration 4. Extinguishment occurred with flow rates from 4.09 to 12.59 grams/second. Flow rates from 2.63 to 3.62 grams/second failed to extinguish the fire.

To further decrease turbulence from the fume hood operation, the front bricks were replaced with a plastic shield (Figure 5). Immediately after the two tests performed with Halon 1211 (Test Numbers 93 and 94), agent dripped out of the nozzle following closure of the solenoid. This prevented accurate measurement of the agent flow as determined by weighing the apparatus. Only Halon 1211 was used with this configuration. Extinguishment was obtained with flow rates from 7.87 to 14.41 grams/second. Flow rates of 2.27 to 5.25 grams/second were ineffective. It is interesting that the highest ineffective flow rates of Halon 1211 with this configuration (5.25 and 4.61 grams/second) were higher than the lowest effective flow rate for HCFC-22 with Configuration 4 (4.09 grams/second).

Several experiments were run with the solenoid and needle valve interchanged (Figure 6). These tests showed that the solenoid must come before the needle valve for a steady, regulated flow. Placing the needle valve before the solenoid allows pressure to build up. Once the solenoid is turned on, a large surge of gas occurs. This surge then diminishes to the level controlled by the needle valve, a phenomenon which causes inconsistent flow. These changes proved less successful than the valve configuration used in the apparatus as shown in Figure 5.

Since a number of compounds of interest are liquids at room temperature, the apparatus was modified for liquids (Configuration 7) as shown in Figure 7. The needle valve was removed and a liquid sample injection port was added between the sample cylinder and the gas gauge. The only other modifications were a series of nozzle changes. Nozzles were changed to determine if flow rates could be controlled by varying the sample cylinder pressures and the nozzle. Different nozzles were used for Test

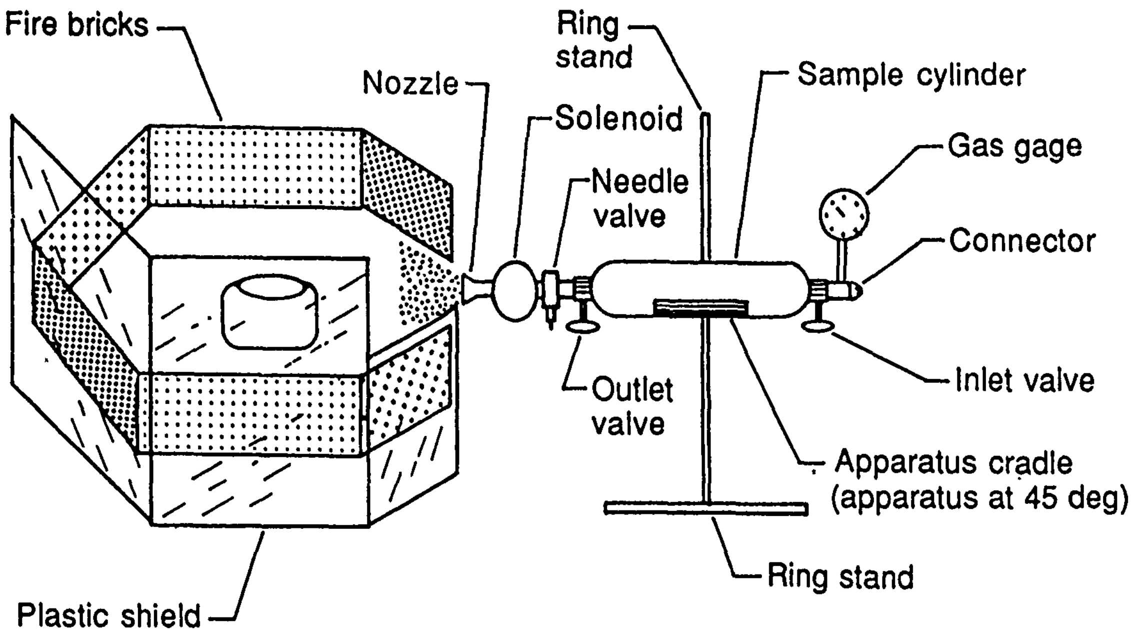

Figure 6. Laboratory-Scale Discharge Extinguishment Apparatus, Configuration 6.

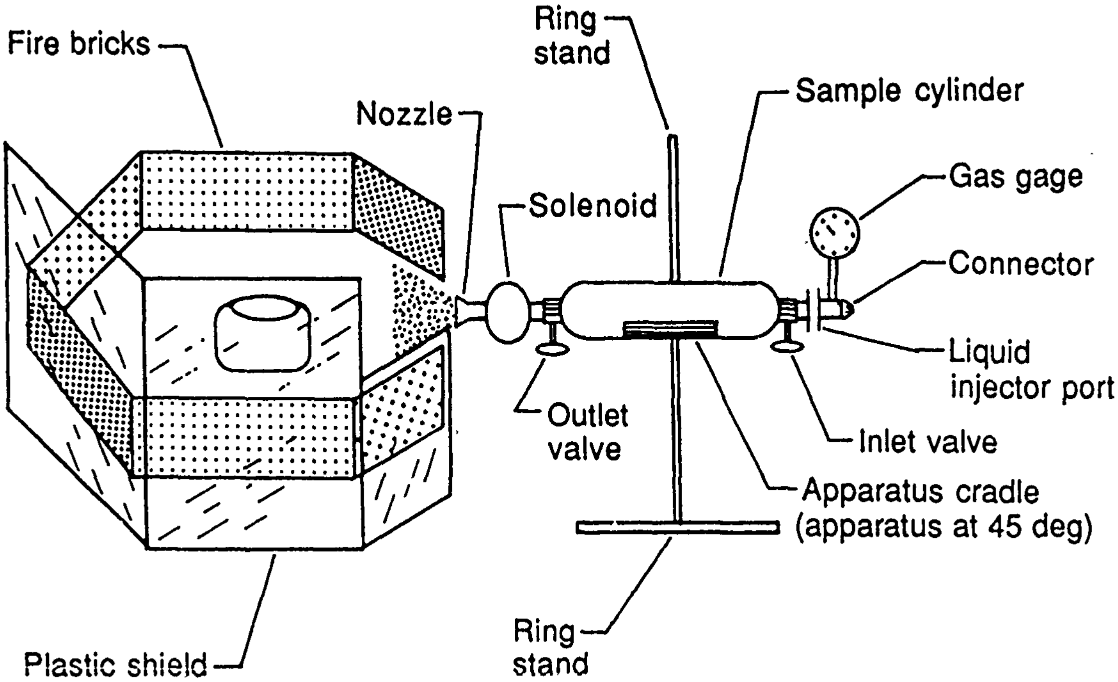

Figure 7. Laboratory-Scale Discharge Extinguishment Apparatus, Configuration 7.

Number 102, Test Numbers 103 through 105, and Test Numbers 106 through 108. Halon 2402 was selected as the liquid standard for evaluation of the apparatus.

Ten-fold higher flow rates were needed for extinguishment by Halon 2402 with this configuration than were required for Halon 1211 or even HCFC-22 with the other apparatus configurations; however, no direct comparison can be made. The need for much larger flow rates may be due to the nozzles used.

C. CONCLUSIONS

The discharge extinguishment apparatuses had accuracy and consistency problems. Agent continued to flow after the solenoid was closed. This phenomenon caused inaccurate weight measurements and flow rate calculations. Removal of the discharge tubing helped to alleviate this problem, but it still occurred to some extent. Using a hand-held stopwatch results in human timing errors, leading to additional inaccuracies in the calculated flow rates. The need to remove the apparatus for weighing after each run causes inconsistent positioning, which affects extinguishment results.

Incorporation of a device attached to the solenoid to record the times of opening and closing would help with the timing problem. The placement of a scale underneath the entire apparatus would alleviate the repositioning problem by giving weight readings without having to transport the apparatus to a remote scale. Controlling flow with different nozzle sizes and cylinder pressurizations instead of the needle valve might alleviate the problem of extra agent flow from the needle valve following the conclusion of a test run.

Continued work is needed to find ways to standardize this system. Once the apparatus gives consistent results with Halon 2402, other chemicals can be tested at flow rates similar to those used for Halon 2402. Comparisons can then be made to determine accurately the fire-extinguishing capabilities of other liquid chemicals relative to those for Halon 2402. To expedite work, a decision was made to proceed to small-scale testing and to discontinue work on a laboratory-scale discharge extinguishment test apparatus in the present phase. This apparatus can be refined in future phases as needed.

SECTION IV
SMALL-SCALE DISCHARGE EXTINGUISHMENT TESTING

A. INTRODUCTION

A small-scale test permits the use of larger amounts of agent and a larger fire so that dripping after discharge and timing are not as important. It was also believed that the small-scale tests might give more meaningful results for development of a training agent alternative.

B. FACILITIES

The small-scale discharge extinguishment tests were conducted in the Combustion Engineering Laboratory on Kirtland AFB. This laboratory is a block building with a testing room and a separate control room from which remote-controlled apparatuses were activated and viewing was performed. An elevated hood with an exhaust fan vented fumes from fires and agents. A separate exhaust fan was installed in the ceiling of the testing room to remove any fumes that escaped from the hood.

C. APPARATUS

Two types of agent containers were used, depending on the amount of agent used: 1-liter stainless steel cylinders and 224 ft^3 cylinders. The 1-liter cylinders were fitted with a remotely actuated solenoid valve and a nozzle assembly. The cylinders were inverted and held in place with clamps secured to a weighted pole stand and were placed on a scale to determine weights. Agents were transferred as liquids to these cylinders from 30-pound supply cylinders. Schraeder valves and standard quick-coupling connectors were used to fill test cylinders.

The 224 ft^3 cylinders, weighing 230 pounds, were also placed on a weighing scale during operation. These cylinders were connected with stainless steel tubing to a nozzle assembly. The large cylinders were secured to the wall and located at a distance from the test fires.

A remotely actuated ignitor, consisting of a 1000-volt electric transformer which supplied current through insulated wires to two stainless steel probes, was used to ignite the fuel. The probes were positioned to produce an electric arc when current was passed through them.

D. PROCEDURE

Test fires were conducted with 24 ounces of JP-4 fuel floating on water in a 1 ft^2 heavy gauge steel pan with a cover and wheels. At the start of each test, the fire pan was filled with between 16 and 32 ounces of JP-4 aviation fuel. The exhaust fans were then activated from the control room. The ignitor was remotely activated until the fuel ignited. The fire was allowed to stabilize for 30 seconds before attempting extinguishment. To initiate extinguishment, a solenoid valve on a cylinder was remotely actuated. The time to extinguishment was determined and the solenoid valve was deactivated. The weight loss of the cylinder was determined after allowing fumes to be partially exhausted from the room.

E. RESULTS AND DISCUSSION

All test results are presented in Table 2. A summary of the test results is given in Table 3.

CFC-114 and CFC-11 (only one good test run) extinguished fires. The extinguishment concentration for CFC-114 as measured by cup burner tests in Phase II of this work (Reference 5) was approximately twice that required for Halon 1211 (6.12 percent as compared to 3.04 percent). The times required for extinguishment by CFC-114 in the small-scale discharge extinguishment tests were approximately twice those required by Halon 1211

TABLE 2. RESULTS OF SMALL-SCALE EXTINGUISHMENT TESTS.[a]

Test number	Agent	Amount used, pounds	Extinguishment time, seconds	Comments
1	Halon 1211	0.8	--	Multiple extinguishments
2	Halon 1211	0.4	7.12	
3	Halon 1211	--	--	Extinguisher malfunction
4	Halon 1211	0.4	3.26	
5	Halon 1211	0.2	1.34	
6	Halon 1211	0.1	0.75	
7	Halon 1211	--	--	Bad test
8	CFC-12	1.3	[b]--	
9	CFC-114	1.2	7.81	
10	CFC-114	--	--	Bad test
11	CFC-12	3.0	[b]--	
12	CFC-11	--	--	Insufficient agent
13	CFC-22	1.7	[b]--	20 sec discharge
14	CFC-12	3.6	[b]--	
15	CFC-114	2.2	5	
16	CFC-114	1.1	5	
17	CFC-114	0.8	2.3	
18	CFC-114	--	--	Bad test
19	CFC-114	4.1		Bad nozzle position
20	CFC-114	1.5	10	
21	CFC-114	0.9	8.7	
22	CFC-11	2.4	10	Fuel inerted
23	CFC-22	--	[b]--	

[a]Tests 1 - 18 used a 1-liter cylinder; Tests 19 - 23 used a 224 ft^3 cylinder. A cylinder pressure of 100 $lb/in.^2$ was used in Tests 1 - 13. For Tests 14 - 18, the pressure was held constant at 70 $lb/in.^2$

[b]No extinguishment.

TABLE 3. SUMMARY OF SMALL-SCALE DISCHARGE EXTINGUISHMENT TEST DATA.

Agent	Boiling point, °C	Amount used, pounds	Extinguishment time, seconds	Extinguishment concentration, %[a]
Halon 1211	-3.9	0.28 ± 0.12	3.1 ± 2.1	3.04 ± 0.36
CFC-11	23.8	[b]2.4	[b]10	
CFC-114	3.8	1.28 ± 0.38	6.5 ± 2.4	6.12 ± 0.15
CFC-12	-29.8	[c]---	[c]---	6.68 ± 0.28
HCFC-22	-40.7	[c]---	[c]---	10.98 ± 0.02

[a]Cup burner extinguishment concentrations from Reference 5.

[b]Only one good test.

[c]No extinguishments achieved.

(6.5 seconds as compared with 3.1 seconds). In addition the weights of agent required for suppression by CFC-114 were much higher than those required by Halon 1211 in these small-scale discharge extinguishment tests.

The single small-scale discharge extinguishment test run on CFC-12 indicated a significantly decreased extinguishment capability for CFC-12 and HCFC-22 compared with CFC-114. No extinguishment was obtained with CFC-12 and CFC-22 under the conditions used for the small-scale discharge extinguishment tests. The cup burner tests run in Phase II of this project gave extinguishment concentrations for CFC-12 that were only slightly higher than those for CFC-114. The much poorer performance of CFC-12 here is probably due to the lower boiling point for this agent compared with CFC-114 (Table 3). A low boiling point gives poor streaming characteristics. The small-scale extinguishment test as configured here is a more rigorous test for streaming than was the laboratory-scale discharge extinguishment test, which gave extinguishment with HCFC-22 for several test conditions.

SECTION V

LABORATORY-SCALE TESTS ON A CFC MIXTURE

A. COMMERCIAL CFC MIXTURE

The results performed in this project have indicated that a CFC or a mixture of CFCs could be used as a training agent having a lower ODP than Halon 1211. Since a commercial CFC blend was available, a decision was made to test this material.

Composite Advanced Halon (CAH) was a commercial blend obtained from Sorensen Research Laboratories (P.O. Box 20, Ramsey, Isle of Man, British Isles). The agent was reported to have a good flame penetration ability with the vapors lying on top of a liquid fuel to provide some inertion. CAH contains no bromine. Company literature reported that the extinguishment characteristics of CAH were similar to those of Halon 1211 and not quite as good as those of Halon 1301 in the British 34B test (34 liters of a mixture of aviation fuel and 100-octane gasoline in a circular pan about 6 inches deep to give 2 inches of freeboard). The extinguishment time for CAH in this test was reported to be about 8 seconds.

Composite Advanced Halon (CAH) was a mixture of CFC-11, CFC-12, CFC-113, CFC-114, and a proprietary material called "Homoginol." Information on the nonproprietary components is given in Table 4 (Reference 6). The lower boiling CFCs should give a mixed-CFC system rapid knock-down; the higher boiling constituents may provide some fuel inertion. This specific mixture is no longer available; however, similar mixtures, named NAF and BLITZ, are now marketed by North American Fire Guardian Technology.Inc. (Vancouver, British Columbia, Canada). NAF contains no CFC-113.

The Underwriter's Laboratories' ratings of toxicity of all of the materials except that of CFC-113 are equal to or less than the rating of 5a for Halon 1211. CAH has a variable boiling point; however, since it can be handled at room temperature, it is less volatile than Halon 1211.

TABLE 4. PROPERTIES OF COMPONENTS OF COMMERCIAL CFC BLEND.

CFC	Chemical formula	Molecular weight, amu	Boiling point, °C	ODP	U. L.[a] Group
11	CCl_3F	137.4	23.8	1.00	5a
12	CCl_2F_2	120.9	-29.8	0.90	6
113	CCl_2FCClF_2	187.4	47.6	1.09	[b]4 - 5
114	$CClF_2CClF_2$	170.9	3.8	0.93	6

[a]Underwriter's Laboratories' classification of comparative life hazard of gases and vapors (Reference 7).

[b]Much less toxic that Group 4 but more toxic than Group 6.

B. INITIAL INVESTIGATION

At the time of this study, the composition of CAH was not fixed. Different formulations of CAH were available. Two aerosol cans containing samples of the "domestic" formulation of CAH were obtained from Sorensen Research Laboratories for an initial investigation.

Fire extinguishment tests were conducted with the supplied aerosols using JP-5 fuel and a 6-inch square pan. The aerosol cans supplied gave a good to excellent throw range.

In the first test, the fire was given a 30-second preburn. A small amount of agent was sprayed over the entire fire. The flames were immediately extinguished. The spray of agent was continued 3 seconds after extinguishment. The fuel was inerted to reignition by an open flame for 30 seconds.

In the second test, the fire was allowed a 30-second preburn. A small amount of agent was sprayed in one corner of the fire pan. The vapors spread across the pan and extinguished the flames. It was not necessary to spray the agent over the entire pan to effect extinguishment. This very small amount of agent did not provide fuel inertion.

The very early examination of the material indicated an excellent throw and significant extinguishment ability. The fuel inertion appeared to be very good. However, comparison tests with common halon agents are needed to assess extinguishment ability.

C. CUP BURNER TESTS

Cup burner tests were conducted on CAH using both the domestic formulation and an "advanced formulation," also obtained from Sorensen Laboratories. The apparatus used is described in Reference 5. JP-4 fuel was used. The procedures reported in Reference 5 were used for testing Halons 1211 and 1301. Since CAH is a nonazeotropic mixture, the concentration of components in the gas phase varies during evaporation, a characteristic that makes cup burner testing difficult. Accordingly, the procedure used in the cup burner tests on CAH had to be modified from those used for the halon controls.

A 15-milliliter aliquot of CAH was injected into an evacuated 300-milliliter stainless steel cylinder. The cylinder was heated to 93 ^{o}C to ensure that all components of the CAH were vaporized. This produced a pressure of 215 lb/in.^{2} (1482 kPa). The gas stream from the cylinder was allowed to flow through an FM102-05S rotameter flow meter to measure the flow rate. No condensation occurred during passage through the rotameter. The results are presented in Table 5.

TABLE 5. CUP BURNER TEST RESULTS.

Test no.	Flame suppression concentration, volume %
	Halon 1301
1	2.44
2	2.38
3	2.33
average	2.38
	Halon 1211
1	2.61
2	2.61
3	2.61
average	2.61
	CAH, Domestic Formulation
1	4.86
2	4.91
3	4.91
average	4.87
	CAH, Advanced Formula
1	4.76
2	4.76
3	4.76
average	4.76

These cup burner results show that CAH requires a concentration approximately twice that required by Halons 1301 and 1211 to effect extinguishment. However, as indicated earlier, discharge characteristics may be at least as important as extinguishment concentration in determining the effectiveness of an agent delivered by streaming. The advanced formulation of CAH may require a slightly lower concentration than the domestic formulation.

D. FUEL INERTION TESTS

1. Inertion Concentration

A series of tests to investigate the inerting action of the domestic formulation of CAH was performed. The small-scale inertion test used a [illegible] 19-inch diameter round stainless steel pan with a depth of 0.375 inch and an area of 8 square inches. For each test, JP-4 fuel was measured into a glass beaker, and sufficient CAH was transferred by buret into the beaker to bring the total volume to 10 milliliters. The mixture of fuel and CAH was stirred with a glass rod and poured into the metal pan. A Bunsen burner was pass over the mixture with the flame touching the surface. If the mixture did not ignite, the flame was immediately passed over the mixture again. If the mixture ignited, new mixtures were prepared in which the percentage of CAH was increased in increments of 0.10 milliliters, until no ignition was obtained. The flame was passed over the mixture twice for each change in agent concentration. The results, given in Table 6, show that CAH will inert JP-4 fuel at a concentration of 14 percent under the conditions used here. A similar test for Halon 2402 gave a JP-4 inertion concentration of 10 percent (Reference 8).

TABLE 6. JP-4 INERTION RESULTS.

CAH concentration, volume percent	Observations
10	Mixture ignited on first pass of burner
20	No ignition with either first or second pass
15	No ignition with either first or second pass
13	Mixture ignited on second pass and burned 3 seconds
14	No ignition with either first or second pass

2. Inertion Time

The inertion time was determined by preparing a mixture at the lowest percentage of CAH required to inert the JP-4 (14 percent by volume) and allowing the mixture to sit in an open fume hood with air passing over it. Mixture containers of two different sizes were used. Both were 3.1975 inches in diameter; however, the larger container was ten times deeper than the smaller. The mixture volume used for the larger container was 100 milliliters; that used for the smaller container was 10 milliliters. Every 5 minutes, a Bunsen burner was passed over the mixture twice. If the mixture did not ignite, it was tested again 5 minutes later. When ignition occurred, the holding period obtained was recorded.

With the smaller container, the JP-4 ignition was obtained after 5 minutes on the first pass of the burner. Halon 2402 exhibited an inertion time of 10 minutes under the same conditions (Reference 8). With the larger container, no ignition was observed after 5, 10, and 15 minutes. After 20 minutes, ignition was obtained on the first pass of the burner. The difference is due to the larger volume to surface area ratio for the larger container.

SECTION VI
CONCLUSIONS AND PROJECTED PHASE IV PLAN

A. CONCLUSIONS

The very limited laboratory work on streaming characterization indicates that photographic methods would provide an acceptable and cost-effective method for determining and documenting drop-size distributions during discharge of halon-like agents. A number of other techniques have been reported; however, none are as inexpensive and easily run as the method demonstrated here.

A laboratory-scale discharge extinguishment test was designed and constructed during this phase, and a number of configurations were tested using control agents. Although this apparatus was not completely successful, sufficient work was performed to demonstrate the usefulness of this technique for characterization of extinguishment by agents delivered by streaming. It is planned that this apparatus will be optimized and used in future work on halon replacements. Note that no laboratory-scale discharge extinguishment apparatus has been reported previously.

The small-scale discharge extinguishment tests verified the expectation that for agents delivered by streaming, extinguishment is highly dependent on boiling point. These results indicate that a mixture of CFCs and/or HCFCs could provide an acceptable training agent, if the boiling point were kept sufficiently high to offset the inherently lower fire suppression ability of these materials. Such blends would provide a training agent with a lower ODP than that of Halon 1211.

Laboratory tests indicated that a blend of CFCs could provide a temporary replacement agent for Halon 1211 in firefighter training. Such an agent would still be regulated under the Montreal Protocol; however, the ODP would be significantly lower than that of Halon 1211, and the environmental impact of Air Force firefighter training operations would be significantly reduced. On the other hand, nontechnical considerations must be included in any decision to use a temporary agent containing regulated materials.

B. PHASE IV PLAN

Class B pool fire field tests of selected CFC and HCFC agents will be performed during Phase IV of this project. Both medium-scale and large-scale tests will be conducted. An important requirement is the survey and compilation of toxicity and environmental data.

1. A brief survey of generally available CFCs and HCFCs will be made with particular emphasis on toxicity and environmental characteristics.

2. Medium-scale tests involving pool fires having areas from 4 to 28 square feet will made on selected CFCs, HCFCs, and/or blends.

3. Large-scale pool fire tests from 100 to 300 square feet will be performed on selected materials. These tests will employ handheld extinguishers and 150-pound wheeled units.

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