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DEPARTMENT OF THE ARMY
CORPS OF ENGINEERS



Report 1341

SMALL-SCALE EVALUATION OF BROMO-FLUOR
(ETHYL BROMIDE-DICHLORODIFLUOROMETHANE
MIXTURE) AND OTHER MIXTURES AS FIRE
EXTINGUISHING AGENTS

Project 8-76-04-003

28 January 1954

ENGINEER RESEARCH
AND
DEVELOPMENT LABORATORIES



THE ENGINEER CENTER
AND
FORT BELVOIR, VIRGINIA

ENGINEER RESEARCH AND DEVELOPMENT LABORATORIES
CORPS OF ENGINEERS
UNITED STATES ARMY

Report 1341

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Project 8-76-04-003

28 January 1954

Submitted to

THE CHIEF OF ENGINEERS, U. S. ARMY

by

The Commanding Officer
Engineer Research and Development Laboratories
Corps of Engineers, United States Army

Prepared by

W. P. Lebans
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TABLE OF CONTENTS

<u>Section</u>	<u>Title</u>	<u>Page</u>
	ABSTRACT	v
I	INTRODUCTION	1
	1. Subject	1
	2. Background	1
	3. Personnel	2
II	INVESTIGATION	2
	4. Evaluation Procedure	2
	5. Extinguisher Used	4
	6. Agent Formulation Charged	4
	7. Other Test Conditions	4
	8. Results of Tests	4
III	DISCUSSION	7
	9. Performance	7
	10. Future Plans	7
IV	CONCLUSIONS AND RECOMMENDATION	8
	11. Conclusions	8
	12. Recommendation	8
	APPENDIX	9

REVISION FOR ERDL REPORT 1341

<u>Page</u>	<u>Paragraph</u>	<u>Line</u>	
1	Footnote 2	1	"marked" to "marketed"
5	Column 1	1	"Halon 2002" to "Halon 2001"
5	Column 1	5	"Halon 2002" to "Halon 2001"
7	10	5	...oxide to establish their relative merits as "knock- down" agents in aircraft fire fighting.

ABSTRACT

This report covers an evaluation of ethyl bromide in mixture with dichlorodifluoromethane for extinguishing incipient Class B, liquid fuel fires. The evaluation was made using bromotrifluoromethane, a mixture of dichlorodifluoromethane and methyl bromide, and mixtures of ethyl bromide and bromotrifluoromethane (halon 1301) as the comparators.

The report concludes that the Bromo-Fluor, ethyl bromide and dichlorodifluoromethane mixture, is not an effective agent for hand portable fire extinguishers, and that, as a basic fire fighting material, it is not as effective as bromotrifluoromethane or methyl bromide.

The report recommends that no further consideration be given to ethyl bromide mixtures as fire extinguishing charges for hand portable fire extinguishers.

SMALL-SCALE EVALUATION OF BROMO-FLUOR
(ETHYL BROMIDE-DICHLORODIFLUOROMETHANE
MIXTURE) AND OTHER MIXTURES AS FIRE
EXTINGUISHING AGENTS

I. INTRODUCTION

1. Subject. This report covers evaluation of ethyl bromide as a fire extinguishing agent component, in mixture¹ with dichlorodifluoromethane² (halon 122), for extinguishing incipient Class B, liquid fuel fires. The evaluation was made using bromotrifluoromethane³ and a mixture of dichlorodifluoromethane and methyl bromide as the comparators. Mixtures of ethyl bromide and bromotrifluoromethane (halon 1301) were also evaluated.

The authority for conducting this work is contained in Project 8-76-04-003, "Fire Extinguishing Agent, Improved, Self-Contained." A copy of the project card is included in the appendix to this report.

2. Background. Prior to World War II, vaporizing liquids used as fire extinguishing agents included carbon tetrachloride (halon 104), methyl bromide (halon 1001) and carbon dioxide. Methyl bromide was, however, never extensively used as a fire extinguishing agent in the United States because of its high toxicity. (It was used as a rodenticide fumigant.) Just prior to, or during, the war, I. G. Farben, AG, developed a formulation of chlorobromomethane (halon 1011) for use as a fire extinguishing agent, which became known to the Corps of Engineers upon termination of World War II. In view of this development and wartime progress in this country in the field of fluorine chemistry, a research and development project was undertaken in which it was proposed to evaluate the fire fighting effectiveness of a number of halocarbon type compounds, including chlorobromomethane and those containing fluorine (since the uses of the "Freon" type agents in refrigeration and aerosols had demonstrated the high degree of chemical inertness possible in such compounds). Work conducted in this research and development project

1. Proprietary name for the mixture of ethyl bromide and dichlorodifluoromethane, as marketed by the Société Industrielle D'Extinction Scientifique (SIDES) in France, is Bromo-Fluor.
2. Dichlorodifluoromethane is produced and marked by E. I. du Pont de Nemours and Company, under the trade name of Freon 12.
3. Use of bromotrifluoromethane (halon 1301) as a fire extinguishing agent is a development of ERDL. See ERDL Report 1177 or NFPA Quarterly, Vol. 2, pp 119-131, Oct 51.

has been reported in previous Engineer Research and Development Laboratories Reports: "Vaporizing Liquid Fire Extinguishing Agents," Report 1177, 18 August 1950; "Demonstration Tests of Winterized Carbon Dioxide Fire Extinguishers," Report 1249, 8 August 1952; and "Investigation of Two Halogenated Hydrocarbons as Inhibitors on the Flammability of Ethylene Oxide," Report 1309, 20 July 1953.

In the previous work, the particular suitability of bromotrifluoromethane for military application has been demonstrated. The investigation currently reported consists of a brief series of practical tests comparing bromotrifluoromethane (halon 1301) with a proprietary agent formulation. The Engineer Research and Development Laboratories received reports of tests conducted in France and Belgium on Bromo-Fluor (or Di-Fluor, as it is known in Belgium) through an American representative of the Société Industrielle D'Extinction Scientifique (SIDES). SIDES is the holder of French patent claims on the Bromo-Fluor⁴ formulation. One such test, conducted at Orly Airport on 25 March 1952, resulted in successful extinguishment of a hydrocarbon fire approximately 70 by 25 ft (23 by 8 m) in 13 sec, using about 45 lb (20 kg) of the Bromo-Fluor agent.

Subsequent to these reports, it was deemed desirable to make small-scale tests with bromotrifluoromethane and with a mixture of dichlorodifluoromethane and methyl bromide, which is also covered by SIDES patent claims.

SIDES developed Bromo-Fluor to meet requirements for a fire extinguisher agent of low toxicity and, at the same time, good extinguishment abilities, using ethyl bromide as the extinguishing agent and dichlorodifluoromethane as the "atomizing" agent.

3. Personnel. Tests were conducted by A. N. Williams, Group Leader; E. A. Helms, Fire Test Fighter; and J. M. Hayden, Chief, Fire Test Station. Collation of the data and preparation of the report were accomplished by W. P. Lebens, under the supervision of J. E. Malcolm, Chief, Agents and Techniques Section, Fire Fighting Branch.

II. INVESTIGATION

4. Evaluation Procedure. The test fire used in these tests was essentially the Standard B2 tub fire, as used by the Underwriters' Laboratories, in which a steel tub, having a 2-ft (61-cm) diameter, was filled with water to a point $10\frac{1}{2}$ in. (26.7 cm) from the top of the tub and 2 qt (1.9 liters) of motor fuel (74 Octane)

4. Approximately 70 percent ethyl bromide and 30 percent dichlorodifluoromethane by weight.

was floated on the water. A burning period of 20 sec was allowed before initiating extinguishment by the unit under test. The type of test fire used is shown in Fig. 1.

Each extinguisher was held in one position during discharge, with the nozzle angled over the edge of the tub, so that the method of application would be consistent for each test.



202-1-151



202-1-149

Fig. 1. Test of mixture consisting of 70 percent ethyl bromide (halon 2001) and 30 percent bromotrifluoromethane (halon 1301). Top: initiating extinguishment; extinguisher charged with ethyl bromide-bromotrifluoromethane mixture. Bottom: same type fire after 3-sec extinguisher application; intensity has not been significantly changed. Time required for extinguishment with bromotrifluoromethane, alone, is about 1.5 sec.

5. Extinguisher Used. Units of a modified version of the 69-cu-in. (1.15 liters) Walter Kidde Model bromotrifluoromethane extinguisher were used in the tests.

6. Agent Formulation Charged. The formulations charged into the test extinguisher are presented in Table I.

The less volatile component (i. e., the preliminary charge) was first charged into the extinguisher unit described in paragraph 5, and then the dispersing component, as indicated in Table I, was charged. All units were then pressurized with nitrogen gas to give a pressure of 400 psig (28 kg per cm²) at 70 F (21 C).

Table I. Extinguisher Charges

Formulation	Weight of Primary Agent Charged		Weight of "Dispersing" or Low Boiling Point Agent Charged	
	(lb) ^a	(kg)	(lb)	(kg)
Bromo-Fluor (CH ₂ CH ₃ Br-CF ₂ CL ₂)	2.00	(0.91)	0.75	(0.34) ^b
Ethyl Bromide Bromotrifluoromethane	2.00	(0.91)	0.75	(0.34) ^c
Methyl Bromide Dichlorodifluoromethane	2.00	(0.91)	0.75	(0.34) ^b
Bromotrifluoromethane	2.75	(1.25)	-	-

a. Measured to the nearest 1/2 ounce

b. CF₂CL₂

c. CF₃Br

7. Other Test Conditions. Tests were conducted in the open air on a clear day, at ambient temperature of 50 F (10 C) and with a wind velocity of 0 to 5 mph (8 km per hr).

8. Results of Tests. Results of tests are shown in Table II. The ethyl bromide and bromotrifluoromethane mixture was evaluated by four tests. Two trials were failures, with the extinguisher being completely discharged on the fire. Average extinguishment time of 10 sec on successful trials was noted, with an application rate of 4 oz per sec (112 g per sec). Results are shown in Fig. 1.

Of the four trials made on Bromo-Fluor, no extinguishments were made. Average time for complete discharge of the unit was

Table II. Performance of Halon Mixtures as Extinguishing Agents

Composition of Mixture ^a	Net Amount Used (lb)	(oz) ^b	(kg)	Discharge Time (sec)	Remarks
Ethyl Bromide, Halon 2002 (C ₂ H ₅ Br) and Bromotrifluoromethane, Halon 1301 (CF ₃ Br)	2	10.0	(1.19)	18.6	Test fire extinguished in first two tests. No extinguishment in 20 sec and total discharge in final tests.
	1	5.0	(0.47)	9.0	
	2	11.0	(1.22)	20.0	
	3	-	(1.37)	20.0	
Ethyl Bromide, Halon 2002 (C ₂ H ₅ Br) and Dichlorodifluoromethane, Halon 122 (CF ₂ Cl ₂) (Bromo-Fluor)	2	15.0	(1.29)	20.0	No extinguishments accomplished on any of the four test fires. The unit was completely discharged against each fire.
	2	12.0	(1.24)	20.0	
	2	13.0	(1.26)	20.0	
	2	11.0	(1.22)	20.0	
100-percent Bromotrifluoromethane, Halon 1301 (CF ₃ Br)	-	5.5	(0.15)	1.4	Test fire extinguished in eight tests; insufficient agent remained to extinguish fire in last test.
(Extinguisher was not recharged during any phase of the test. Total amount used in nine trials was 2 lb, 11 oz (1.22 kg).)	-	4.5	(0.13)	1.2	
	-	9.0	(0.25)	1.4	
	-	5.0	(0.14)	1.0	
	-	2.5	(0.07)	0.8	
	-	3.0	(0.08)	1.0	
	-	5.0	(0.14)	1.0	
	-	3.0	(0.08)	0.8	
	-	5.5	(0.15)	3.0	
Methyl Bromide, Halon 1001 (CH ₃ Br) and Dichlorodifluoromethane, Halon 122 (CF ₂ Cl ₂)	1	3.0	(0.46)	3.4	Test fire extinguished in five tests; no extinguishment in final test.
	-	10.0	(0.28)	1.4	
	-	10.0	(0.28)	2.0	
	-	14.0	(0.39)	2.6	
	1	9.0	(0.72)	6.0	
	-	6.0	(0.17)	-	

a. All mixtures were charged into modified Walter Kidde extinguishers and pressurized with nitrogen gas to 400 psi (28 kg per cm²) at 70 F (21 C).

b. Measured to the nearest 1/2 ounce.

20 sec. The application rate was approximately 10 oz per sec (280 g per sec). Results are shown in Fig. 2.

For comparison purposes, nine trials were made with 100-percent bromotrifluoromethane, using the same extinguisher, with no recharging at any stage of the test. Eight extinguishments were effected, with the last trial resulting in failure due to insufficient agent remaining in the extinguisher. Average extinguishment



202-1-150



202-1-148

Fig. 2. Test of Bromo-Fluor mixture consisting of 70 percent ethyl bromide (halon 2001) and 30 percent dichlorodifluoromethane (halon 122). Top: initiating extinguishment, with the extinguisher charged with Bromo-Fluor. Bottom: extinguisher exhausted after attempt to extinguish test fire with Bromo-Fluor, with failure to put out fire.

time was 1 to $1\frac{1}{2}$ sec, with an application rate of 4 oz per sec (112 g per sec).

Tests were also made with a mixture of methyl bromide and dichlorodifluoromethane. Six trials were made, five of which resulted in successful extinguishment. The last trial failed because insufficient agent remained in the extinguisher to effect the extinguishment. Average extinguishment time was $2\frac{1}{2}$ sec, with an application rate of 8 to 10 oz per sec (224 to 280 g per sec).

III. DISCUSSION

9. Performance. In no case did ethyl bromide mixtures perform as satisfactorily as the methyl bromide mixture with dichlorodifluoromethane. Bromotrifluoromethane displayed the greatest effectiveness in the tests.

Ethyl bromide was previously found to be less toxic than methyl bromide; however, it is more flammable. Flammable limits of 6.75 to 11.25 percent by volume are reported⁵, as compared to 13.5 to 14.5 percent by volume for methyl bromide⁵. Previous evaluations of ethyl bromide indicated flammability of this compound in actual attempts in extinguishing the tub type fire.

Previous studies indicated that dichlorodifluoromethane is at least as effective as carbon tetrachloride, which is a common vaporizing liquid fire extinguishing agent.

The success of this Bromo-Fluor agent on the large-scale fires appears to be a result of the relatively high rates of application used, and good fire approach techniques, with multiple points of application. Rates of up to about 5 lb per sec have evidently been used.

10. Future Plans. Under separate project, it is proposed to compare bromotrifluoromethane (halon 1301) with such agents as methyl bromide (halon 1001), chlorobromomethane (halon 1011), dichlorodifluoromethane (halon 1202), "Bromo-Fluor", and carbon dioxide to establish relative merits in this type fire fighting. Though tests to date indicate superiority of halons 1301 and 1202, the relative advantage with the other "comparator" agents should be demonstrated in this application so that justification of this use of one of the more costly agents may be made.

5. N. I. Sax, Handbook of Dangerous Materials, Rheinhold, 1951.

IV. CONCLUSIONS AND RECOMMENDATION

11. Conclusions. It is concluded that Bromo-Fluor, ethyl bromide and dichlorodifluoromethane mixture, is not an effective agent for hand portable fire extinguishers, and that, as a basic fire fighting material, it is not as effective as bromotrifluoromethane or methyl bromide.

12. Recommendation. It is recommended that no further consideration be given to ethyl bromide mixtures as fire extinguishing charges for hand portable fire extinguishers.

APPENDIX

AUTHORITY

SECURITY CLASSIFICATION - UNCLASSIFIED

RESEARCH AND DEVELOPMENT PROJECT CARD (NEW PROJECTS)		2. SEC. U	3. PROJ. NO. 8-76-04-003
1. PROJECT TITLE FIRE EXTINGUISHING AGENT, IMPROVED, SELF-CONTAINED		4. OLD PROJ. NO. ME766	
4. BASIC FIELD OR SUBJECT Fire Fighting		6. REPORT DATE 30 Sept 47	
7. SUB FIELD OR SUBJECT SUB GROUP Fire Fighting			
8. COGNIZANT AGENCY Office, Chief of Engineers	12. CONTRACTOR AND/OR LABORATORY Engr. Res. & Dev. Laboratories Perdue Research Foundation	CONTRACT/W. O. NO. W44-009ENG507	
9. DIRECTING AGENCY Engr. Res. & Dev. Div., MO, OCE	10. REQUESTING AGENCY Office, Chief of Engineers	17. EST. COMPL. DATES RES. July 48 DEV. July 48 TEST Dec. 48	
11. PARTICIPATION AND/OR COORDINATION	13. RELATED PROJECTS	14. DATE APPROVED 31 January 1947 by WDGS	
	15. PRIORITY 2-A	16.	
19. Item No. 1083, CETC Meeting #169		17. EST. EVAL. DATES 48 15 48 10 T 50	
20. REQUIREMENT AND/OR JUSTIFICATION There is a requirement for a fire extinguishing agent equal to or superior to methyl bromide in its effectiveness in the extinguishment of fires, and no more toxic than carbon tetrachloride. This development may result in an item of material that possesses such marked superiority over existing items that complete replacement will be justified.			
21. BRIEF OF PROJECT AND OBJECTIVE			
a. REFERENCES:			
(1) Report of Preliminary Tests of "CB" Fire Extinguishing Agent by Engineer Research and Development Laboratories 14 August 1946.			
b. OBJECTIVE:			
(1) Development of an improved, self-contained fire extinguishing agent to replace existing agents used in combating flammable liquid and electrical fires.			
c. MILITARY CHARACTERISTICS:			
(1) The agent shall be suitable for use in combating Class "B" and "C" fires.			
(2) It shall not be more toxic than carbon tetrachloride.			
(3) It shall be suitable for use at temperatures from 120 degrees F to at least minus 50 degrees F, and as near to minus 70 degrees F as possible			
(4) It shall not deteriorate when transported, or when stored for periods of time up to five years, under any climatic conditions.			
(5) It may be produced in quantity within reasonable cost limits, and with existing production facilities.			
(6) Its corrosive effects shall not be greater than that of standard carbon tetrachloride fire extinguisher fluid.			
(7) It shall be a non-conductor of electricity.			
d. DISCUSSION:			
(1) Preliminary studies of fire extinguisher media have included a study of a new agent captured in Germany which appears to have desirable characteristics as a fire extinguishing agent. This agent has a chemical nomenclature of "monochloromonobromomethane" which, for simplicity, is being called "CB". A limited quantity has been produced and tested. The results of these preliminary tests have			
22. JRDB	SN.	PC.	IC & P.
			X. I. C.

JRDB FORM 18, 1 APR 1947

WDGRD-

PAGE 1 OF 2 PAGES

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d. DISCUSSION (Continued):

- (1) proved encouraging.
- (2) The agencies interested in this project in addition to the Corps of Engineers are the Army Ground Forces, Air Force, and the Navy.

e. PROJECT PLAN:

- (1) Funds will be provided to a qualified research agency to search the chemical compound field for an agent equal or superior to methyl bromide in its effectiveness in extinguishing fires, and which is no more toxic than carbon tetrachloride. Any agents which laboratory tests indicate are worthy of trial will be procured for thorough testing by the Engineer Research and Development Laboratories or other qualified agency. If necessary, an extinguisher for applying the agent will be developed.
- (2) The Perdue Research Foundation is to explore the Flourine field to determine the suitability of oven flourine compounds as fire extinguishing agents.

VDGD-

PAGE 2 OF 2 PAGES

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APPROVAL OF

Report 1341

SMALL-SCALE EVALUATION OF BROMO-FLUOR
(ETHYL BROMIDE-DICHLORODIFLUOROMETHANE
MIXTURE) AND OTHER MIXTURES AS FIRE
EXTINGUISHING AGENTS

28 January 1954

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8-76-04-003

22 APR 1954

SUBJECT: Transmittal of Report 1341, Small-Scale Evaluation of
Bromo-Fluor (Ethyl Bromide-Dichlorodifluoromethane Mixture)
and Other Mixtures as Fire Extinguishing Agents

TO: Chief of Engineers
Department of the Army
Washington 25, D. C.
ATTN: Chief, Engineer Research and Development Division

1. Transmitted herewith is Report 1341, "Small-Scale Evaluation of Bromo-Fluor (Ethyl Bromide-Dichlorodifluoromethane Mixture) and Other Mixtures as Fire Extinguishing Agents", dated 28 January 1954, which was prepared by the Technical Staff of the Engineer Research and Development Laboratories.

2. The report, with its conclusions and recommendations, is approved.

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H. MILLETT
Colonel, CE
Commanding

SUBJECT: Transmittal of Report 1341, Small-Scale Evaluation of Bromo-Fluor
(Ethyl Bromide-Dichlorodifluoromethane Mixture) and Other Mixtures
as Fire Extinguishing Agents

ENGNC (8-76-04-003)
(22 Apr 1954) TECRD SB

1st Ind.

Office of the Chief of Engineers, Washington 25, D. C. 30 April 1954

TO: Commanding Officer, Engineer Research and Development Laboratories
Fort Belvoir, Virginia

1. The recommendation, paragraph 12, page 8 of Report 1341, "Small Scale Evaluation of Bromo-Fluor (Ethyl Bromide-Dichlorodifluoromethane Mixture) and Other Mixtures as Fire Extinguishing Agents", is approved.

2. The proposed distribution list, a copy of which is inclosed, with additions and deletions as shown also is approved. Copies of the report for The Assistant Chief of Staff, G-4 and Headquarters, Army Field Forces will be forwarded by this office.

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Engr Research and Development Div

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