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TOXICITY

A STUDY OF VAPORIZABLE EXTINGUISHANTS

FILE → FIRE EXTINGUISHING AGENTS

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Midland, Michigan*

JANUARY 1960

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WRIGHT AIR DEVELOPMENT DIVISION

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A STUDY OF VAPORIZABLE EXTINGUISHANTS

David L. Engibous
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The Dow Chemical Company
Midland, Michigan

JANUARY 1960

Aeronautical Accessories Laboratory
Contract No. AF 33(616)-5838
Task No. 61331

WRIGHT AIR DEVELOPMENT DIVISION
AIR RESEARCH AND DEVELOPMENT COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

FOREWORD

This report was prepared for the Aeronautical Accessories Laboratory, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio, by The Dow Chemical Company, Midland, Michigan. This "Study of Vaporizable Fire Extinguishants" was performed under Contract No. AF 33(616)-5838, Task No. 61331. Work commenced on this contract July 1, 1958, and was completed in August, 1959. Lt. E. A. Stecca, of the Fire Protection Equipment Section, Base Equipment Branch acted as the project engineer.

The work was carried out at The Dow Chemical Company under the direction of D. L. Engibous, of the Chemical Engineering Laboratory. T. R. Torkelson performed the toxicological studies that are reported. Acknowledgements are due to C. DeWaele who assisted in the literature survey and to J. W. Barber, B. A. Russell, H. DeShon and K. A. Allswede who assisted in the experimental work. Acknowledgement is also due to Major E. F. Westlake, of the Biochemistry Section, Physiology Branch, Aerospace Medical Laboratory, WADC, who made many constructive comments concerning the toxicity section of this report.

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ABSTRACT

Bromochloromethane, or CB as it is commonly known, is now used as the vaporizing liquid fire extinguishing agent on crash trucks as a supplement to mechanical protein foam, which is the primary means of combatting flammable liquid fires. CB is recognized to present a toxicity problem of ill-defined magnitude. Other agents have been proposed as replacements for CB and this study evaluated the following compounds for this purpose:

Dibromodifluoromethane	Halon 1202; Freon 114 Br
Bromochlorodifluoromethane	" 1211
Bromotrifluoromethane	" 1301
1,2-Dibromotetrafluoroethane	" 2402

CB was used as a standard of comparison throughout.

A comprehensive survey and analysis of existing literature on these agents which covers effectiveness, toxicity, physical properties, test methods, and dispensing techniques is included. The report discusses the current Air Force requirements of vaporizing liquid extinguishants and how these five agents satisfy these requirements. The different toxicity mechanisms are described and a complete acute toxicity picture on a concentration versus time basis is presented. Results of actual fire tests performed in this study and tests by previous investigators are given and evaluated.

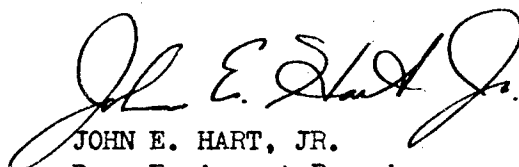
As a result of this study, Bromochlorodifluoromethane (Halon 1211) appears as a promising agent for optimum ground fire protection. Bromochlorodifluoromethane is about a ten fold toxicity improvement over CB. In addition, it is slightly more effective in extinguishing ability and is more stable on long term storage.

Further work including more complete pyrolyzed toxicity studies is suggested to establish the applicability of this agent to Air Force fire protection problems. Fabrication of dispensing nozzles designed specifically for Bromochlorodifluoromethane is also necessary.

PUBLICATION REVIEW

The publication of this report does not constitute approval by the Air Force of the findings or conclusions contained herein. It is published only for the exchange and stimulation of ideas.

FOR THE COMMANDER:



JOHN E. HART, JR.
Base Equipment Branch
Ground Support Equipment Division
Aeronautical Accessories Laboratory

SUMMARY AND RECOMMENDATIONS

All of the five agents in this study meet the current Air Force requirement of high extinguishing effectiveness although there are differences among them. The effectiveness depends to a large extent upon the fire geometry and this seems to be the main reason for the differences in the relative effectiveness of the agents as reported by different investigators. In general, Halons 1301, 1202 and 2402 rank about on a par, with Halon 1211 slightly below them but above Halon 1011. Halon 1301 is not as effective in fire situations where reflash is a problem because of its low boiling point (-72°F.).

Of several possible hazards, the hazard presented by a short term inhalation exposure to a high concentration of the vaporizing liquid agent is the most important. The chronic toxicity and the skin absorption toxicity are not problems to the user of these five agents for fire extinguishing purposes. The toxicity of the products of thermal decomposition of the agents has been placed out of perspective by experimental work which involved overly severe conditions. These thermal decomposition products have adequate warning properties to minimize this hazard. Analysis of reported fatalities from carbon tetrachloride, which is more toxic than any of the five agents studied here, indicate the compound itself and not its decomposition products is the major toxicant. No reported fatalities from the use of Halon 1011 (CB) were found.

The Air Force currently has in Halon 1011 (CB) an effective secondary agent that presents very little health hazard. There is no health hazard from CB in the outdoor exposures experienced in ground fire applications and a hazard exists only in those cases where personnel are subjected to forced exposure to high concentrations of CB for a relatively long period of time.

Of the five agents in this study, only two (Halon 1301 and 1211) meet the current Air Force requirement of a toxicity approaching that of CO_2 . Halons 1301 and 1211 are less toxic than CO_2 in the natural state on a weight per unit volume basis. In addition these two agents are the most thermally stable of the five and therefore present the least problem as far as decomposition products are concerned.

While the toxicity problem presented by the pyrolysis products of an agent is minor as compared to that of the agent itself, no practical work along these lines is reported for Halon 1211. Some work is reported by the Army

Chemical Center ⁵⁶ in which the agent was passed through an iron tube at 800°C but Halon 1211 was not one of the agents used in the more significant studies of the toxicities of various agents in the presence of actual gasoline fires. Such a project was beyond the scope of this investigation but it should be performed. Since the thermal stability of Halon 1211 approaches that of Halon 1301 the results are expected to be of the same order of magnitude as those found for Halon 1301.

Halons 1301 and 1211 are superior to the others as far as storage stability is concerned, although all five agents meet this requirement with the proper choice of materials of construction.

Halon 1011 is presently the lowest in cost of the five agents and will remain so. Also, Halon 1011 can be shipped in non-returnable drums while Halons 1211 and 1301 require cylinders.

The maximum range obtainable is a direct function of the boiling point of the agent. The optimum agent pattern for the largest number of fire geometries is a long elliptical cone.

Halon 1211 is suggested as best satisfying all the requirements of an optimum vaporizing liquid agent for ground fire protection. It also offers the possibility of an effective, low toxicity agent that can be used in a low-pressure fixed in-flight system for aircraft. Fabrication of dispensing nozzles that are designed specifically for Halon 1211 would seem to be the next step in the development of this agent. In view of the fact that fire geometry is such an important variable in the evaluation of an agent, further fire tests by other investigators using Halon 1211 are recommended.

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INTRODUCTION

Bromochloromethane (CB) was introduced into the German armed forces during World War II as an improved vaporizing liquid fire extinguishing agent. It was more effective than carbon tetrachloride and less toxic than methyl bromide, both of which were then in common use. At the end of the war, various Allied technical missions investigated and reported the German experience with this agent. As a result, considerable development work was done in this country which led to the adoption of this material by the Air Force as the standard agent for aircraft fire extinguishing systems. Shortly thereafter it was adopted as the secondary agent on all water-foam aircraft fire fighting trucks. Bromochloromethane has performed well in this application as far as effectiveness is concerned but is criticized strongly from a toxicity standpoint. This fear of the toxicity has prevented maximum exploitation of the potential effectiveness of this agent.

A large amount of research work, which was aimed at developing improved vaporizing liquid agents, has been reported throughout the literature in the past ten years. A comprehensive study at Purdue University⁵ under an Army ERDL contract indicated several fluorine containing compounds which were more effective and less toxic than CB.

The purpose of the present study was to evaluate four of these compounds and to compare them with CB in ground fire applications. Many factors were to be included in this evaluation but the most important were toxicity and application techniques. While ground fire applications were to be of primary interest in this study, consideration was to be given to the other areas where vaporizing liquids are used, namely, portable hand fire extinguishers and fixed in-flight systems on aircraft.

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SECTION I
GENERAL THEORY OF FIRE EXTINGUISHMENT

Fire is the chemical combination of an oxidizing and a reducing agent resulting in such a large thermal energy release that visible flame and/or smoke result. The oxidizing agent is usually atmospheric oxygen but other examples would be nitric acid, nitrates, chlorates, and fluorine. The reducing agent can be wood, paper, gasoline, hydrazine, ammonia, alcohol, hydrogen, or any other combustible material. Normally, fires are considered to fall into one of three general classes although any given fire can be a combination of these classes, which can be described as follows:

1. Class A fires involve solid materials, usually cellulosic in nature, such as wood, paper and cloth. The accepted mechanism of combustion involves the thermal decomposition of the solid into flammable vapors as in the case of wood, or the direct combustion of the solid as in the case of carbon or charcoal.

2. Class B fires involve flammable liquids, and the oxidation reactions are usually considered to take place in the vapor state. Since many of these liquids exert sufficient vapor pressure at normal temperatures to provide a flammable region above the liquid surface, the preliminary heating that is necessary to ignite wood is not required to initiate combustion of these materials. In the case of low volatility flammable liquids (heavy oils, for example) combustion can occur only after some preliminary heating has vaporized sufficient material to form a flammable concentration in the region above the liquid.

3. Class C fires differ from the others in that electricity is present. The fire itself is a Class A and/or Class B fire. The main requirement of an extinguishing agent for Class C fires is that it be electrically non-conducting, both for the safety of the operator and to prevent greater involvement because of electrical arcing.

Classically, fires can be extinguished by one or more of three general mechanisms. First, the combustible material can be cooled to a temperature so low that flammable vapors no longer evolve or the surface is taken below the ignition temperature. This is the basic mechanism by which water extinguishes Class A fires. The second general method involves smothering the fire by lowering the oxygen or the fuel concentration in the surrounding area to a level that will not support combustion. This is the basic mechanism by which carbon dioxide extinguishes fires although this material also has a significant cooling effect as well.

The third method consists of separating the fuel from the oxidizer either by removing one or by mechanically separating the two. This is the major mechanism of mechanical protein foam on Class B fires although foam also exerts a cooling effect because of its water content.

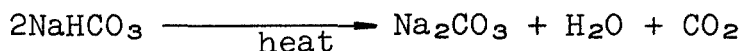
For many years the three mechanisms described above, either separately or in combination, were considered to be adequate explanations of how all fires were extinguished. The vaporizing liquids were thought to act by a combination of all three mechanisms, the most important of which was the lowering of the oxygen concentration of the air by displacement. They also cooled by absorbing from the fire the heat required to vaporize them. Further, it was proposed that since the molecular weights of these materials were so high in comparison to air that the vapors of these agents formed a protective layer over the fuel that excluded the entrance of additional oxygen.

Most investigators no longer accept the above explanations for the effectiveness of vaporizing liquids. First of all, if these agents acted by lowering the oxygen content of the air, one would expect all vaporizing liquid agents to be about as effective as carbon dioxide or nitrogen on an equimolar (equal volume) basis. However, they are much more effective on this basis than the inert gases. Secondly, the amount of heat removed from the system by the vaporization of the agent is usually negligible in comparison to the heat given off by the combustion process. Finally, while the heavy vapors may act as a protective blanket above the fuel in some cases, the vaporizing liquid agents are effective under conditions where this is obviously not true, e.g., fires in an aircraft power plant.

The best explanation for the behavior of vaporizing liquid agents in extinguishing fires seems to be primarily chemical in nature with the cooling and dilution mechanisms of secondary importance. This explanation is based upon the fact that free radicals, e.g., the hydrogen atom, are known to exist in flames and that the combustion reactions that lead to flame propagation are chain reactions involving free radicals. It is not known with certainty which of the free radicals that can be postulated are chain carriers, but it is known that the halogens and halogen containing compounds react with free radicals of this type. If then, the halogen compound reacts with a chain carrier free radical and terminates the chain, the flame propagation ceases. This theory is widely held by most investigators today. A comprehensive literature review in this subject is given by Fryburg ¹.

This theory is likely to remain just that until the mechanisms of combustion are completely understood for hydrocarbons and other fuels. At present, only the mechanism of the oxidation of hydrogen, the simplest fuel, is at all well understood. The reader can appreciate the complexities of the problem since these free radicals only exist at flame temperatures. Modern spectrographic techniques show considerable promise along these lines, however; and progress is slowly being made. A survey of recent work dealing with fundamental knowledge of fires and fire extinguishment is given by Friedman and Levy.^{2, 3}

While the present survey deals only with five vaporizing liquid agents, it is of interest to note that the effectiveness of dry chemical (sodium bicarbonate powders) also cannot be explained by the three simple mechanisms of cooling, smothering, or mechanically separating the fuel from the oxidizer. It was formerly believed that this agent extinguished fires because the material itself decomposed in the presence of a flame according to the following reaction:



This reaction is endothermic, i.e., it absorbs heat, and the reaction products include steam and CO_2 which were thought to be the actual extinguishants. Experimental work, however, indicated that dry chemical is more effective than can be explained by the amount of steam and CO_2 available upon complete decomposition of the bicarbonate. Also, it was established that only a small fraction of the bicarbonate decomposed in actual fire situations.

The explanation for the effectiveness of dry chemical again seems to be a chemical interference with the flame reactions. This may be due, in part, to the large surface area of these powders trapping the chain carrier free radicals in a manner similar to the "wall effect" experienced with many free radical reactions. Recent work⁵⁷ at the Naval Research Laboratory on actual fires established that potassium bicarbonate is twice as effective as the commercially common sodium compound. This can only be explained on a chemical basis of interference with the flame chemistry.

Of course the above may not be the sole mechanism by which dry chemical works since it is known to have a shielding effect which prevents the radiant energy of the flame from being fed back to the fuel and increasing the rate of vaporization.

SECTION II
ASSETS AND LIABILITIES OF COMMON AGENTS

A. Water is the most common fire extinguishing agent. It is almost universally available at very low cost, and it exhibits the largest cooling effect of any fire extinguishing agent. Water has a higher specific gravity than most flammable liquids and so tends to spread fires of this type. It conducts electricity and therefore is dangerous to the operator using straight stream application in a Class C involvement. Other limitations of this agent include the fact that it freezes at 32°F. and its use on fires may cause damage.

Its past use in straight stream application has been limited primarily to Class A fires. Water-fog, however, is effective in some Class B situations, particularly for controlling unconventional propellant fires.

B. Mechanical Protein Foam is water that has been treated with chemicals and air so as to lower its specific gravity to below that of all flammable liquids. Its use is normally restricted to Class B fires since water is more effective on Class A fires, and most Air Force foam trucks can readily switch from foam to water. It is the only Class B agent that combines a large cooling effect with permanence of extinction. It is relatively cheap, very effective, and like water, non-toxic. Most foam today is a mechanical protein foam which is made by entraining air into water that contains hydrolized proteins which give the foam stability. Foam does not have particularly fast knock-down time and offers operational problems at low temperatures because of freezing. This agent is not effective on burning fuel that is spilling out of a leaking tank or on fires inside a structure where a foam blanket cannot be laid.

C. Carbon Dioxide is suitable on Class B and C fires. It combines a cooling effect with a smothering action. The agent is a mixture of gaseous and solid CO₂ (snow) at -78°C. (-108°F.) as it reaches the fire. It is cheap, causes no damage in use, and relatively non-toxic although concentrations above 10% can lead to unconsciousness. CO₂ is not particularly effective, particularly in outdoor situations, and its use normally calls for high pressure containers. It requires pressurization with nitrogen to obtain satisfactory discharge at -65°F. The fuel can reignite readily after extinguishment is secured with this agent.

D. Dry Chemical is commonly sodium bicarbonate powder treated with stearates to keep it free flowing. It is a

very effective agent on Class B and C fires. It is more effective, for hydrocarbon fuel fires, than any other agent with the exception of the best of the vaporizing liquids. Dry chemical is relatively cheap and considered non-toxic. A problem of "non-compatibility" with mechanical protein foam exists since dry chemical causes rapid breakdown of the foam blanket. This is due to the stearates that have been added to the bicarbonate. Elimination of this material results in a "compatible" dry chemical. All the storage and caking problems of compatible dry chemical are not completely resolved as yet, but progress is being made.

Technique of application is critical with dry chemical, and a fuel fire has a tendency to reflash. Reignition can also occur readily after extinguishment is secured. Dry chemical is not normally considered suitable for Class A fires. The use of dry chemical leaves a non-conducting residue which may damage fine machinery and cause electronic equipment to become inoperative.

E. Vaporizing Liquids. Only general remarks will be made here since a more detailed discussion of the assets and liabilities of five vaporizing liquid agents on an individual basis appears later in this report. Vaporizing liquids are effective on Class B and C fires, and those agents with high boiling points (such as bromochloromethane) are also suitable for small Class A fires. Vaporizing liquids exhibit varying degrees of fuel inhibiting capabilities, not possessed by dry chemical, CO₂, or water in most instances. Normally, the vaporizing liquids present no freezing problem and no residue problem. The cost of these agents varies from moderate to high and the toxicity problem varies from severe (methylbromide) to very low (bromotrifluoromethane and bromochlorodifluoromethane).

SECTION III

PHYSICAL PROPERTIES OF VAPORIZING LIQUIDS

The most important physical properties of the five agents that comprise this study appear in Table I. The Halon system of nomenclature as well as other names for these agents appear in Appendix II, page 90. A large part of this physical property data was obtained by the Purdue Research Foundation in a comprehensive research program aimed at finding improved extinguishing agents. Their work is described in reference 5 which, unfortunately, is not readily available. The material has been reproduced in many other documents, however. The E. I. duPont de Nemours Company has also measured many of the physical properties of these agents ⁶, ⁷ and some were determined in the course of the present study.

For the sake of simplicity the Halon numbers of the five agents will be used hereafter in this report. Only those physical properties that are the most important are given here. References 5, 6, 7, 8 and 9 give more complete information.

It can readily be seen that these five agents encompass a wide range of boiling points, which is the property that does most to describe these agents in a physical sense. Halon 1301 is very near to CO₂ (b.p. -78°C.) in this respect although its vapor pressure at 130°F. is much less than that of CO₂ which has a pressure of 1050 psig at its critical temperature of 88°F. Halons 1011 and 2402 are similar to carbon tetrachloride as far as physical handling is concerned. Halon 1211 has a boiling point near to that of methyl bromide (b.p. + 3.6°C.) while Halon 1202 acts like a slightly more volatile carbon tetrachloride.

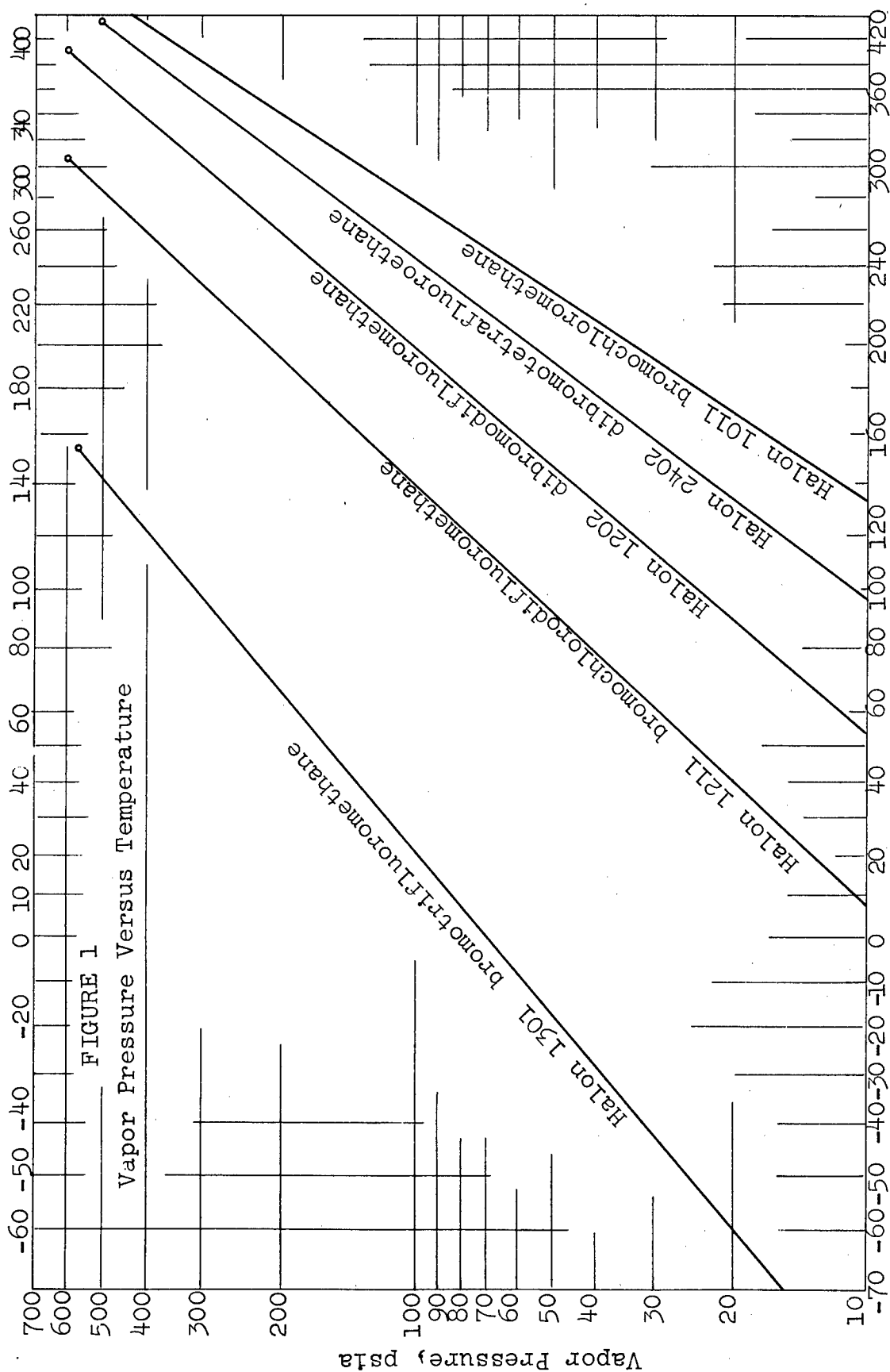
The vapor pressure-temperature relationships of the five agents that comprise this study are given in Figure 1. The critical points of all the agents are shown in this figure with the exception of Halon 1011 which is beyond the limits of the chart.

TABLE I

PHYSICAL PROPERTIES OF SELECTED AGENTS

Chemical Name	Bromochloro- methane 1011 CH ₂ BrCl	Dibromodifluoro- methane 1202 CBr ₂ F ₂	Bromochloro- difluoromethane 1211 CBrClF ₂	Bromotrifluoro- methane 1301 CBrF ₃	Dibromotetra- fluoroethane 2402 CBrF ₂ CBBrF ₂
Halon Number	1011	1202	1211	1301	2402
Chemical Formula	CH ₂ BrCl	CBr ₂ F ₂	CBrClF ₂	CBrF ₃	CBrF ₂ CBBrF ₂
Molecular Weight	129.4	209.8	165.4	148.9	259.8
Boiling Point, °C.	67.0	22.8	-4.0	-57.9	47.4
Atmos. Press., °F.	153.0	73.0	24.8	-72.0	117.3
Freezing Point, °C.	-88.9	-141.5	-160.5	-174.4	-110.5
Freezing Point, °F.	-125.4	-223.0	-257.0	-282.0	-166.8
Critical Temp., °C.	296.8	198.8	153.8	67.4	214.5
Critical Temp., °F.	567.0	390.0	309.0	153.5	418.0
Critical Press., psia.	953.	593.	595.	574.	500.
Critical Density, lbs./gallon	5.75	6.96	5.94	6.2	6.58
g./cc.	0.69	0.836	0.713	0.745	0.790
Density at 70°F., lbs./gallon	16.1	19.0	15.25	13.1	18.0
(liquid) g./cc.	1.93	2.28	1.83	1.57	2.16
Density at 130°F., lbs./gallon	15.4	17.9	14.15	10.4	17.1
(liquid) g./cc.	1.85	2.15	1.69	1.25	2.05
Heat of Vaporization, cal./gm.	56.4	28.3	32.0	28.2	25.0
at 760 mm. press. Btu./lb.	101.5	50.9	57.6	50.8	45.0
Vapor Press. at 130°F. psig.	0.	25.	75.	435.	4.
Vapor Press. at -65°F. psig.	0.	0.	0.	2.5	0.

Temperature, °F.

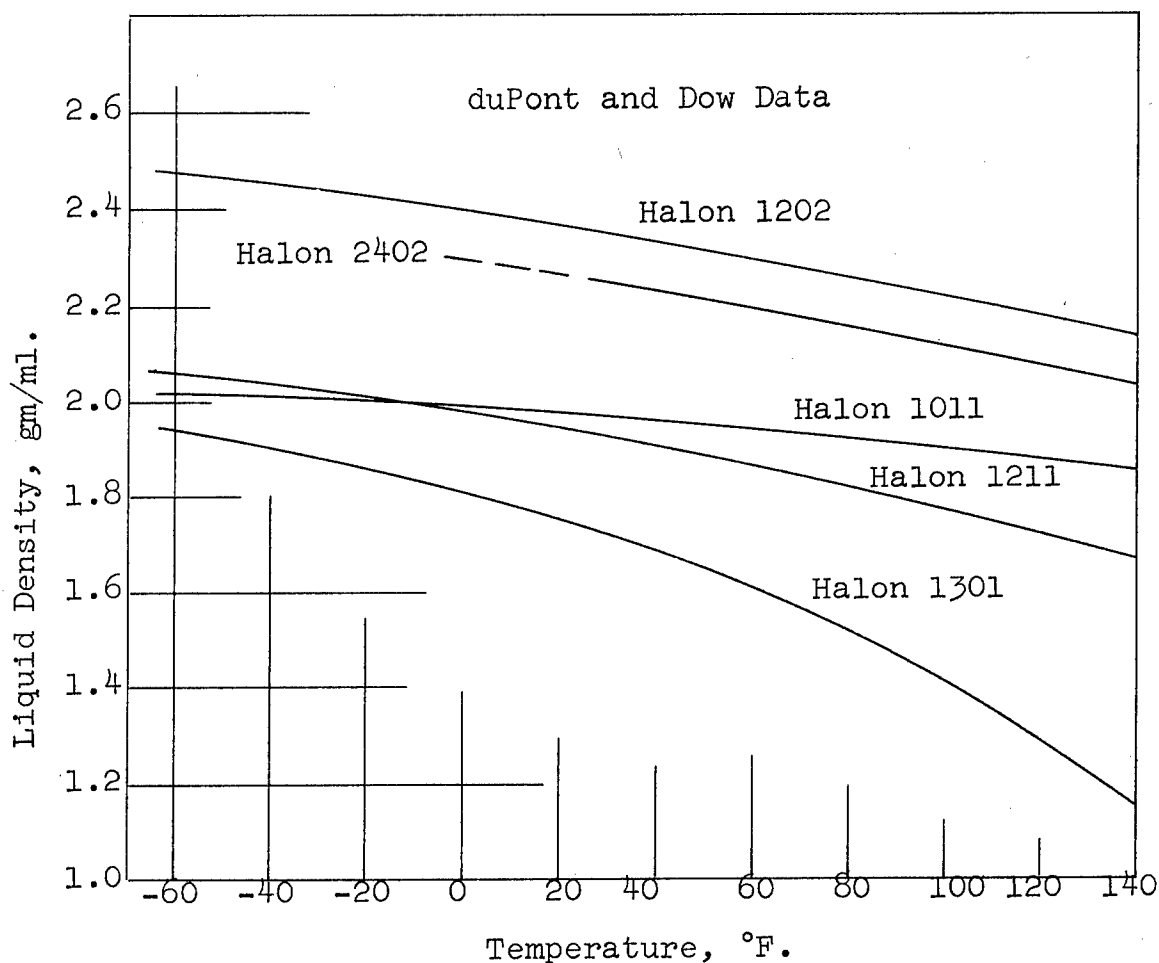


Temperature, °F.

The liquid density of a fire extinguishing agent under autogenous pressure is of importance in the shipment of the material and in the design of the extinguishing container. ICC regulations specify that a shipping container cannot be liquid full at 130°F. and military use of these materials ordinarily occurs over a wide temperature range -65°F. to +130°F. being frequently specified. Densities of these compounds (in the liquid state) are therefore given over a temperature range and appear in Figure 2.

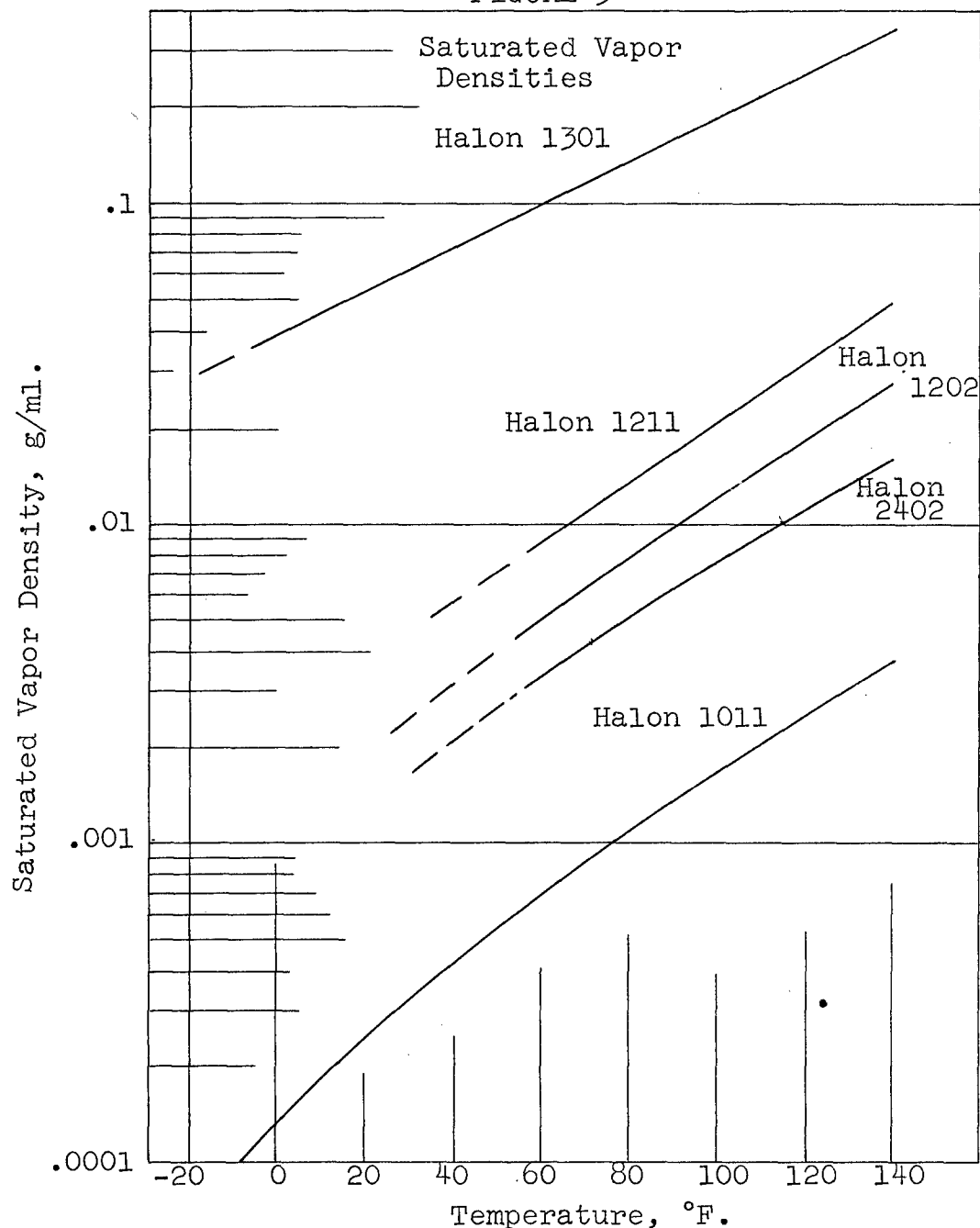
FIGURE 2

Density of Liquid Agents



The saturated vapor densities of the agents appear in Figure 3. The vapor density is dependent upon the amount of agent existing in the vapor state and therefore Halon 1301, which has the highest vapor pressure, has the highest vapor density. It is of practical interest to note that the vapor density is the measure of the amount of agent vapor left in the extinguishing container at the end of the liquid discharge period. For Halon 1301, this can be 15% of the agent originally charged to the extinguisher.

FIGURE 3



The heat capacities of the liquid and vapor states of these agents are of interest mostly to the loader of extinguishing units. They also can be used in conjunction with the latent heat of vaporization to estimate the relative amounts of liquid and vapor that exist in the discharge stream. Since the sudden release of agent from the container is a flash vaporization, Halon 1301 will be at its boiling point (-72°F.) upon discharge and will be a mixture of liquid and vapor (provided that enough is discharged so that the heat capacity of the line, valve, and nozzle is not sufficient to completely vaporize the agent). Halon 1211 will be a liquid-vapor mixture upon discharge anytime the ambient temperature is above 25°F. At all temperatures above -72°F. , a greater percentage of Halon 1211 will exist in the liquid state upon discharge than Halon 1301. Halons 1202, 2402, and 1011 will normally be almost completely in the liquid state upon discharge. Of course, fine sprays of any of these agents vaporize readily in the presence of the large heat flux from the fires. The heat capacities of the liquid and vapor at constant pressure are given in Table 2. Only one temperature is given for the heat capacity of the vapor, but the variation with temperature over a range of -65 to $+130^{\circ}\text{F.}$ is negligible.

TABLE 2
HEAT CAPACITIES
E. I. DU PONT DE NEMOURS AND DOW DATA

Agent	Heat Capacity of the Liquid in cal/gm $^{\circ}\text{C}$ or Btu/lb/ $^{\circ}\text{F.}$		Heat Capacity of the Vapor-cal/gm/ $^{\circ}\text{C}$ or Btu/lb/ $^{\circ}\text{F.}$
	-40°F.	$+100^{\circ}\text{F.}$	$+70^{\circ}\text{F.}$
Halon 1011	0.172	0.184	
1202	0.137	0.162	0.09
1301	0.167	0.230	0.11
1211	--	0.19	0.11
2402	--	0.150	0.11

More complete information, particularly on Halon 1301, will be found in the duPont "Freon" Technical Bulletin, B-29. An example of a simplified flash vaporization calculation will be found in Appendix III, page 91.

SECTION IV CURRENT AIR FORCE REQUIREMENTS

The current Air Force requirements for vaporizing liquid fire extinguishing agents for ground fire protection may be briefly stated as follows:

1. The agent must be suitable for Class B and C fires.
2. The agent must have high extinguishing effectiveness.
3. The agent must be less toxic than Halon 1011 (Bromochloromethane) and should approach carbon dioxide in this respect.
4. The agent should be stable on handling and on storage for up to five years.
5. The agent must be capable of being used as a liquid.
6. The agent must have a freezing point below -65°F .
7. The agent must be capable of being produced within reasonable cost.

In addition, the agents must have quick knockdown capabilities and be compatible with foam. These requirements appear in the original Exhibit (WCLEG-1-34) and also apply to portable and fixed in-flight extinguishers even though drawn up primarily for ground fires.

Let us consider each of these seven requirements individually as they apply to the five agents under consideration in this study.

A. Suitable for Class B and C Fires

Class B fires involve all flammable liquids although in the vast majority of cases the flammable liquid is a hydrocarbon and then usually gasoline or jet fuel. These latter fuels are responsible for most of the Class B fire hazards in the Air Force today, simply because of the enormous amounts used. Most investigators agree that jet fuel, once ignited, presents about the same fire problem as gasoline, although the jet fuel may be somewhat more difficult to ignite because of a higher flash point.

It has been well established that all five candidate agents are suitable on hydrocarbon fires although with varying degrees of effectiveness. The Purdue Research Foundation investigated the suitability of Halons 1011, 1202, and 2402 on various rocket fuels, e.g., hydrogen,

ammonia, methanol, ethanol, nitromethane, and aniline. Halons 1211 and 1301 were not included in their study but carbon dioxide and methyl bromide were. Their results showed that all the agents exhibited effectiveness on these fuels but that Halon 2402 was the most effective. This work is described completely in reference 10 and summarized in reference 11 which is an NFPA Bulletin that is readily available.

The criterion of suitability of a fire extinguishing agent for Class C fires is that the agent be electrically non-conducting. All five of the agents in this study satisfy this requirement since they all have very high resistivity. The Purdue Research Foundation⁵ measured the resistivity of several fluorocarbons as part of their ERDL contract and found them to range from 1×10^{11} to 4×10^{14} ohm centimeters. ^{*} They attempted to measure the resistivity of Halon 1301 but experienced experimental difficulties and obtained values of 1×10^{10} to 1×10^{14} ohm centimeters. For comparative purposes, the resistivity of mica is in the neighborhood of 1×10^{16} ohm cm.

No data was found on specific measurements of resistivity of the other agents but for practical purposes they can all be considered non-conductors of electricity.

B. High Degree of Effectiveness

1. Previous Work

There are many means of evaluating the effectiveness of any fire extinguishing agent. These methods range from laboratory studies under carefully controlled conditions to fire tests on various "standard" fires. Both methods have their merits and also severe limitations. A common method of evaluating agents in the laboratory is by an explosion buret technique which determines the inhibiting effect of the agent on a fuel-air mixture in the tube. The apparatus used by the Purdue Research Foundation⁵ was a 5.1 cm by 123 cm. glass tube into which different fuel-air-agent mixtures were subjected to an electrical spark to determine flammability. The fuel used was n-heptane for the screening process although other fuels were also studied.

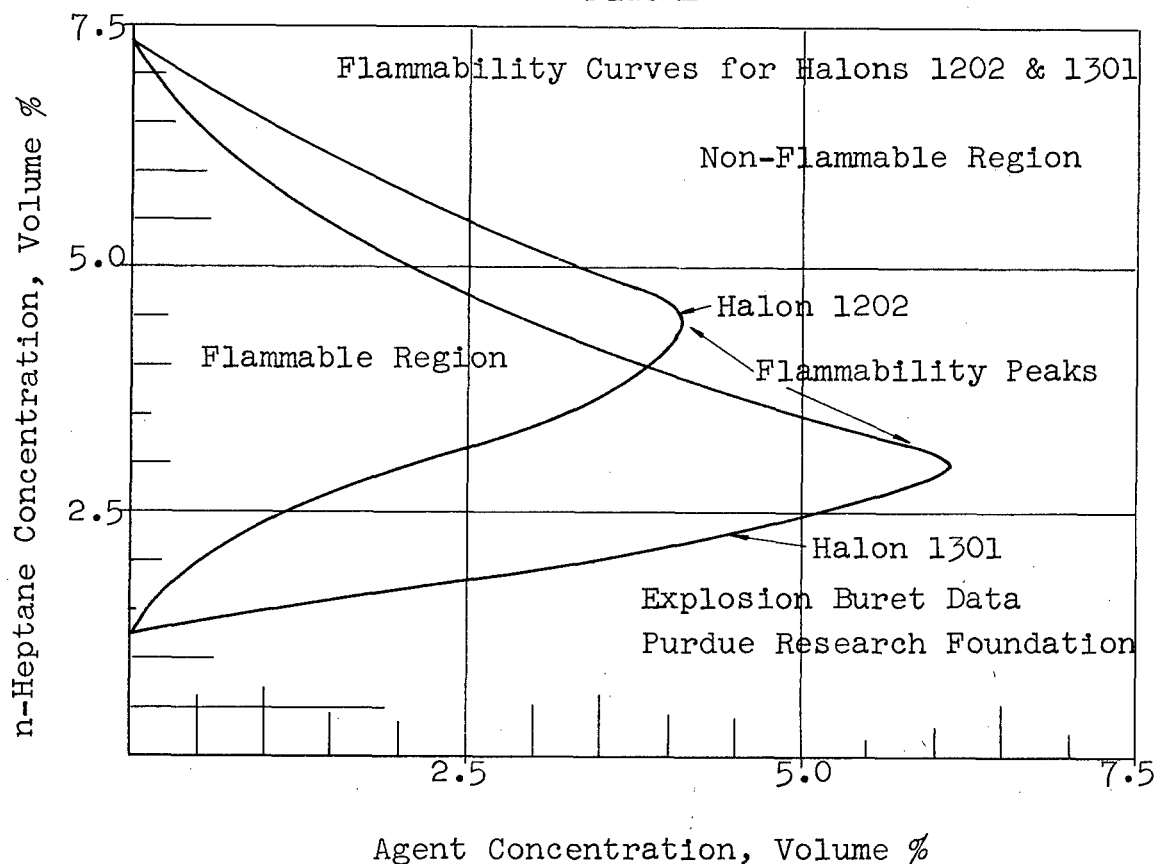
^{*} (When the electrical resistance is in ohms, the length of the conducting medium is in centimeters, the cross sectional area is in square centimeters, the resistivity has the units of $\frac{\text{ohm cm}^2}{\text{cm}}$ or ohm cm.)

This technique results in a so-called flammability curve which is shown in Figure 4. The peak in the flammability curve is that minimum volumetric concentration of the agent at which no mixture of fuel and air is flammable. For the n-heptane air mixture at room temperature and at 300 to 500 mm total pressure, flammability peaks were observed for the five agents being considered here. Some other common agents are given for comparative purposes. Both the volume % and the weight in grams corresponding to this volume % are given.

TABLE 3
FLAMMABILITY PEAKS

Halon	Name	Vol. %	Flammability Peak Wt. of agent, gm.
1202	Dibromodifluoromethane	4.2	39.37
2402	Dibromotetrafluoroethane	4.9	56.87
1301	Bromotrifluoromethane	6.1	40.57
1011	Bromochloromethane	7.6	43.93
1211	Bromochlorodifluoromethane	9.3	68.71
1001	Methyl Bromide	9.7	41.13
104	Carbon Tetrachloride	11.5	79.00
	Carbon Dioxide	29.5	57.94

FIGURE 4



It is of interest to note that since the molecular weight of these materials varies so widely, both the volume % and the weight required to obtain this concentration are important. Carbon dioxide, for example, while relatively ineffective on a volume basis, compares favorably on a weight basis.

Both ERDL and the Purdue Research Foundation realized that the ability of a material to prevent flame propagation did not necessarily correlate well with the ability to extinguish a flame once it had been initiated. As a result some standardized pot test fires were investigated at ERDL. The equipment was a water jacketed container of n-heptane which was ignited and given a thirty second preburn. The agents were admitted at constant flow rates through four fixed inlets one inch above the surface of the fuel. Time to extinguish was then determined. The test setup is described in references 4, 5, 8 and 12 but actual results are not given. Only agents that are gases at room temperature could be studied by this technique. The investigators concluded that the flame suppression studies in the explosion buret were valid measures of agent effectiveness.

The effect of different fuels was considered in the same flame suppression apparatus and while differences were noted, the relative effectiveness of the compounds remained the same for the fuels tested. Unfortunately, of the five candidate agents, only the peak values for Halon 1301 were determined. The data for Halon 1001 (methyl bromide) are shown for comparative purposes in Table 4.

TABLE 4
FLAMMABILITY PEAKS IN VOLUME %
ROOM TEMPERATURE
U. S. ARMY ERDL

<u>Fuel</u>	<u>Halon 1301</u>	<u>Halon 1001</u>
n-Heptane	6.1	9.7
Isopentane	6.3	8.4
Benzene	4.3	8.4
Ethyl Alcohol	3.7	6.2
Diethyl Ether	6.3	7.2
Acetone	5.3	7.3
Ethyl Acetate	4.6	6.8

More information on the effect of fuel was reported by the Purdue Research Foundation on another project. 10, 11 This work was done under an Air Force contract and Halon 1301 was not one of the agents studied, presumably, because

an agent of lower vapor pressure was desired. Again Halon 1001 is available for comparative purposes and the results may be summarized as follows:

TABLE 5
FLAMMABILITY PEAKS IN VOLUME %
PURDUE RESEARCH FOUNDATION

Fuel	Halon 1001	1011	1202	2402	Temp. [★] °F.
Hydrogen	15.5	31.0	34.4	17.3	78.8
Methyl Alcohol	21.0	17.9	20.6	16.8	78.8
Ethyl Alcohol	11.4	8.7	5.8	5.3	266
Nitromethane	18.9	12.4	8.6	4.2	302
Aniline	1.9	1.8	3.2	2.2	392

These agents no longer remain in order in terms of relative effectiveness, probably because of the widely different chemical structures of the fuels used.

Some other flame propagation work of interest is reported by the duPont Company ^{6, 8, 9}. These experiments were performed in a one-inch by thirteen-inch explosion pipette. The electrodes were in the top of the tube, and thus the flame propagation was downward. Forcing the flame to propagate upward is a more severe test of the inhibiting agent and results in more conservative values for the flammability peaks ¹³. A mixture of 9.9 volume % methane and 90.1 volume % air was used in all tests so that the complete flammability curve is not available from this data. Study of Figure 4 makes it obvious that if only one fuel air mixture is used the order of effectiveness can be varied from that obtained by the flammability peak. With these limitations in mind, however, the data still give a measure of relative effectiveness of these agents on methane and are presented here in Table 6.

★ Various test temperatures were required because the boiling points of some of the fuels are so high. This however, introduces another variable as will be evident later.

TABLE 6

AGENT EFFECTIVENESS
E. I. DUPONT DE NEMOURS

<u>Agent</u>		<u>Effectiveness</u>	
<u>Halon</u>		<u>Volume</u>	<u>Weight</u>
<u>No.</u>	<u>Name</u>	<u>%</u>	<u>%</u>
1211	Bromochlorodifluoromethane	0.5	2.9
1202	Dibromodifluoromethane	0.5	3.7
1001	Methyl Bromide	0.8	2.7
2402	Dibromotetrafluoroethane	0.85	7.4
1011	Bromochloromethane	1.0	4.5
1301	Bromotrifluoromethane	1.1	5.6

It is of interest to note how the relative effectiveness as obtained in this system varies from that reported by the Purdue Research Foundation. The rankings of the five agents by the two investigators can be summarized (with the best at the top) as follows:

<u>Purdue Research Foundation</u> ⁵				<u>duPont</u> ^{6, 8, 9}	
<u>Volume basis</u>		<u>Wt. basis</u>		<u>Volume basis</u>	<u>Wt. basis</u>
Halon	1202	Halon	1202	Halon	1211
"	2402	"	1301	"	1202
"	1301	"	1011	"	2402
"	1011	"	2402	"	1011
"	1211	"	1211	"	1301
				"	2402

The major advantages of the explosion tube technique of evaluating agents are that only a small amount of agent is necessary, different fuels can be readily used, and the data are very reproducible if proper precautions are taken with the laboratory apparatus. The accuracy of the resulting data has led several investigators to attempt to correlate the chemical composition of the agent with its flame inhibition effectiveness.

Malcolm ⁴ examined the Purdue Research Foundation data and introduced the concept of "atomic resistivity" for the halogen atoms in the agent molecule. These "atomic resistivities" were determined from trial and error calculations based upon the flammability peaks (in n-heptane) of 52 halogenated materials. It had been known previously that some of the halogens were more effective than others, but this was the first attempt to assign numerical ratings to them. Malcolm's deduced atomic resistivities were:

Fluorine	1
Chlorine	2
Bromine	10
Iodine	16

Using these resistivities it was possible to calculate the flammability peak, thus:

$$\text{Flammability Peak} = \frac{100}{\sum \text{Atomic resistivities}}$$

For example, Halon 1211 has one bromine, one chlorine, and two fluorine atoms in the molecule and would have a calculated flammability peak of

$$\text{F.P.} = \frac{100}{10 + 2 + 1 + 1} = \frac{100}{14} = 7.1 \text{ volume } \%$$

No credit is given in this method for the hydrogen atoms in the molecule.

Belles¹⁴, however, suggests a value for the hydrogen in the molecule. He considers the model of the hydrogen atom reacting with singly halogenated methanes and with ethane. He then assigns relative reactivities (comparable to Malcolm's atomic resistivities) on the basis of the activation energy and an assumed reaction temperature (1550°K). His work may be summarized as follows:

TABLE 7
RELATIVE REACTIVITIES
BELLES, NACA

Reaction	Activation Energy E, cal/mole	-E/RT e	Relative Reactivity
H. + CH ₃ F → CH ₃ . + HF	10,000	0.039	1.0
H. + CH ₃ Cl → CH ₃ . + HCl	8,000	0.075	1.9
H. + CH ₃ Br → CH ₃ . + HBr	5,000	0.198	5.1
H. + CH ₃ I → CH ₃ . + HI	2,000	0.522	13.4
H. + C ₂ H ₆ → C ₂ H ₅ . + H ₂	6,700	0.114	2.9

The flammability peak again is calculated by dividing the sum of the relative reactivities into 100. A comparison of the two methods of calculating the flammability peaks follows:

Agent	Observed Flammability Peak, ⁵	Calculated Flammability Peak	
	Volume %	Malcolm	Belles
Halon 1202	4.2	8.3	7.8
" 2402	4.9	4.2	7.0
" 1301	6.1	7.7	12.3
" 1011	7.6	8.3	7.8
" 1211	9.3	7.2	11.1

In general, the values suggested by Belles predict flammability peaks better for hydrogen containing molecules (provided enough halogen is present to make the compound non-flammable) but worse for completely halogenated compounds than do the empirical values suggested by Malcolm.

Belles introduces the concept of "fuel equivalent of the agent" as a method of rating agents. He argues that the fuel itself is an effective extinguishing agent in a closed system like the explosion buret since a flammable mixture can be rendered non-flammable by the addition of sufficient fuel to exceed the rich limit mixture.* In other words, either a certain number of moles of fuel or agent will inhibit flame and the ratio of these two is the "Fuel equivalent of the agent". The higher this ratio, the more effective the agent. The values for the five agents in this study are as follows:

Fuel Equivalent of Agent
Belles, NACA

Halon 1211	0.39
" 1202	0.55
" 1301	0.61
" 1011	0.61
" 2402	0.69

The total reactivity as defined by Belles correlates better with the fuel equivalent of the agent than with the flammability peaks.

Other investigators have criticized the emphasis placed upon the flammability peak data and argue that the total flammable area underneath the flammability curve is the real measure of agent effectiveness. Coleman and Stark ¹⁵ conclude that a rapid lowering of the rich limit curve with Halon 1011 is the reason this agent is much more effective in actual fire tests than carbon tetrachloride, which does not cause such a rapid decrease of the rich limit curve. The flammability peak for carbon tetrachloride in an n-heptane air mixture is 11.5 volume % as compared to 7.6% for Halon 1011 yet fire tests showed a greater difference in effectiveness than these data would predict.

* Of course this concept has no validity in an open system where there is ready access to air. No one has yet proposed adding gasoline to an outdoor fire in order to exceed the rich limit mixture and thus extinguish it. n-Hexane has been used, however, to suppress fuel-air explosions in fuel tanks ²¹ (a closed system) by exactly this method.

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While there is merit in the theory that the area under the flammability curve is important it is also true that in any actual fire situation probably all concentrations from the rich limit to the lean limit exist simultaneously. Since the most difficult concentration of fuel and vapor to extinguish (ordinarily the lean limit mixture) will determine success or failure of the fire fighter, the flammability peak is probably more important than the area underneath the flammability curve in rating the agents.

Caution should be exercised in attempting to extrapolate laboratory results to practical fires for several reasons. First of all, explosion buret data are themselves empirical in that direction of flame propagation, tube size, and tube wall composition can all be important variables. Secondly, no information on agent application rate, pattern, or range, (all important variables in actual fires) can be obtained from explosion buret data. Because of the practical limitations of laboratory data, most investigators have evaluated different extinguishing agents by extinguishing actual fires. In so doing, a whole host of other variables are introduced and the resulting data are empirical and very limited in general usefulness. A brief list of the variables involved in actual flammable liquid fire tests follows:

1. The flammable fuel used is a variable.
2. The agent is of course the primary variable in any evaluation of agents.
3. The agent application rate is a very important variable and one which, unfortunately, has not been treated as such by all investigators.
4. The agent application pattern is significant.
5. The fire geometry is important. Pan fires are popular but round pans differ from square pans in fire characteristics and shallow pans differ from deep pans.
6. The fuel depth is a variable for those agents which enter the fuel in the liquid phase and exert an inhibiting effect. It is not much of a variable for agents (such as Halon 1301) which are so low boiling that this mechanism does not play a part in extinguishment.
7. Wind plays a part in determining the characteristics of the fire and can either aid or deter extinguishment. In order to eliminate this variable, some investigators have run indoors tests. Resulting data are usually much more

consistent, but in many practical fires wind remains a problem.

8. Ambient temperature is a variable.
9. Application technique, particularly if the human element is present, can be a major variable.
10. Preburn time is a variable if very short or very long times are used.

Some of the most recent and best practical fire studies which included all five of the candidate agents are reported by Ansul²² and duPont 7. Most of the above variables were eliminated in this work but it should be obvious that elimination of a variable by standardizing test conditions also restricts transferring the results to other fire situations. For example, pan fires do not necessarily correlate with spill fires or dripping fuel fires. Unless an infinitely large number of tests are run which include all the variables, this non-applicability of the results will remain a criticism to some degree for all practical fire tests.

The method used in the above studies was based upon determining the minimum quantity of agent required to extinguish a standard fire when applied at the optimum application rate. The standard fire used was a water jacketed test pan, three feet ten inches in diameter. Two inches of a gasoline known as stove and lamp naphtha were placed on a six inch layer of water and given a thirty second preburn. The tests were run in a special fire test building, and as a result the variables of wind and ambient temperature were essentially eliminated. The agent was applied through four nozzles spaced evenly inside the pan at a height of six inches above the fuel and 1 1/2 inches below the top of the pan. Different nozzles, orifice sizes, and agent pressurization (which affects the degree of atomization) were studied and optimum conditions for each agent were determined. The resulting data were presented in graphical form and are reproduced here in Figure 5. In all cases, the area above the line represents extinguishment and the area below represents failure to extinguish. It should be noted that a lot of information is presented in Figure 5 inasmuch as the quantity can be divided by the application rate to obtain application time and consequently extinguishment time since essentially no time lag occurred between extinguishment and agent shut off. A curve showing the relationship of time to quantity of agent necessary to extinguish is reproduced in Figure 6.

FIGURE 5

Agent Application Rate Versus
Quantity of Agent Expended

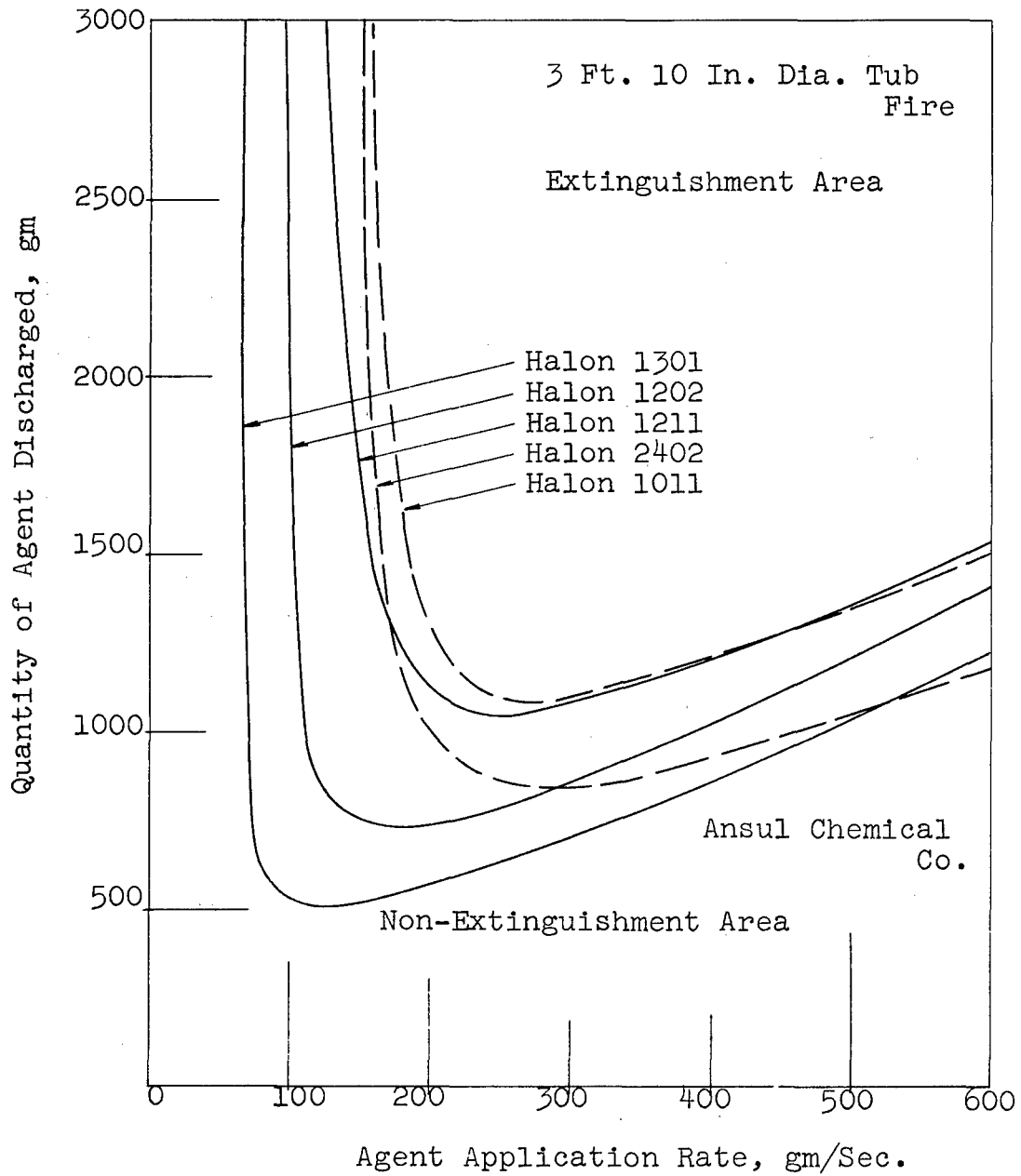
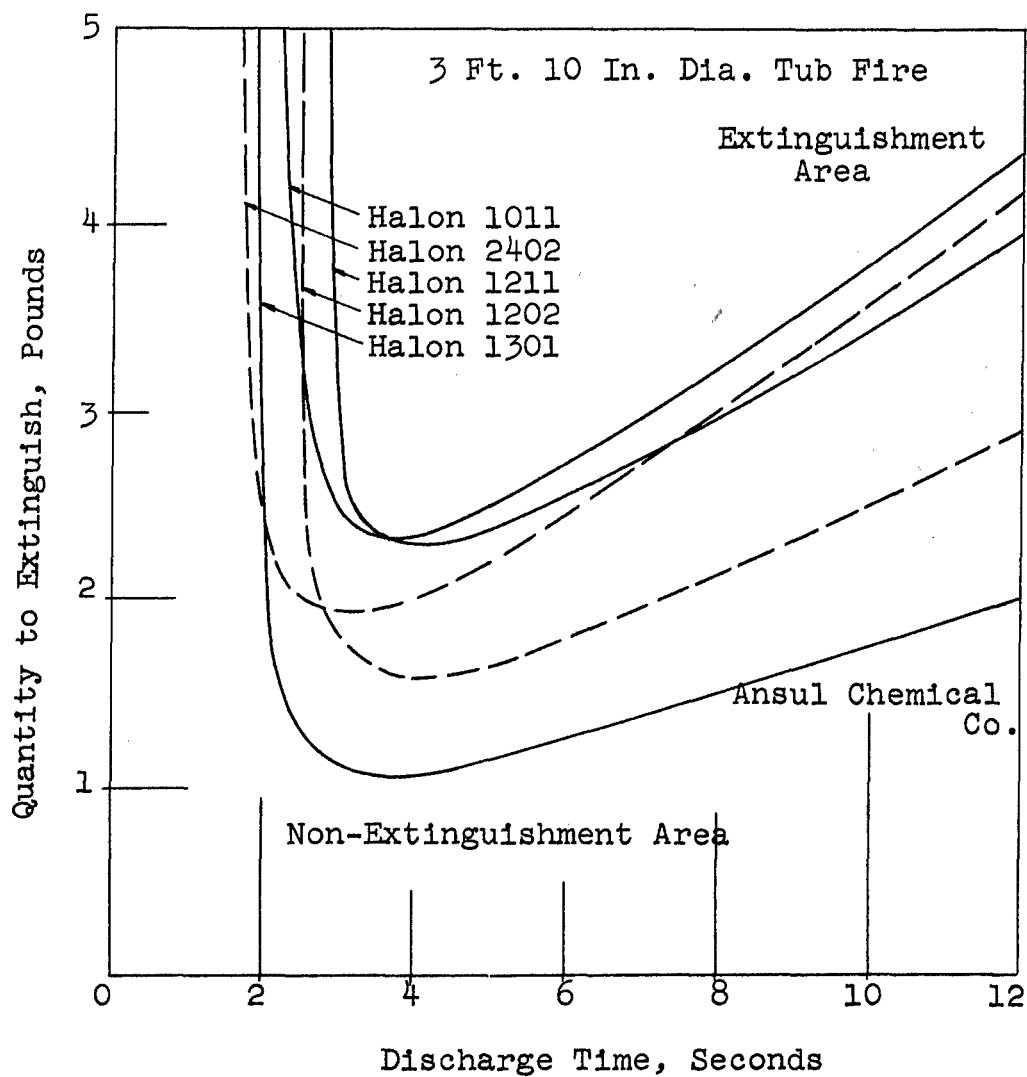


FIGURE 6
Quantity of Agent Required to Extinguish
Versus Agent Discharge Time



As a result of this work effectiveness ratings were presented in tabular form ⁷ for three of the five candidate agents (Halon 1301, 1202 and 1011), and the author has calculated these values for Halons 1211 and 2402 from the published curves. These are weight effectiveness values, and the weight effectiveness values as obtained from flammability peak data are also presented for comparison.

TABLE 8
WEIGHT EFFECTIVENESS RELATIVE TO HALON 1301
ANSUL CHEMICAL COMPANY
PURDUE RESEARCH FOUNDATION

<u>Agent</u>	<u>Fire Tests</u>	<u>Flammability Peak ⁵</u>
Halon 1301	100	100
" 1202	67	103
" 2402	56	71
" 1211	46	59
" 1011	45	92

The differences in the two methods illustrate the difficulties of transposing explosion buret data to an actual fire situation.

Some other effectiveness studies on a high rate discharge system are reported by the Civil Aeronautics Administration Test Station ⁸ at Indianapolis, Indiana. The agents were evaluated on the basis of the weight required to extinguish a standard fire. The data are reported to be accurate to within 0.01 lbs. and the results have been summarized as follows:

TABLE 9
AGENT EFFECTIVENESS ON HIGH RATE SYSTEMS
CAA TEST STATION

<u>Agent</u>	<u>Lbs. Required to Extinguish Standard Fire</u>	<u>Wt. Effectiveness Relative to Halon 1301</u>
Halon 1301	0.10	100
" 1211	0.105	95
" 1011	0.11	91
" 2402	0.12	83
" 1202	0.125	80

On this particular standardized fire no great differences in effectiveness were experienced. The reason for this is probably due to the fact that the agent was applied through a high rate discharge system and therefore the agent application rate was greater than the critical value. Study of the Ansul data as presented in Figure 5

shows that differences in effectiveness of the agents are minimized under high application rate conditions. In other words, if all the agents were applied at 454 g/sec. (1 lb./sec.) to the standard fire used by Ansul, the weight of agent discharged and the weight effectiveness of the agents would be approximately as follows:

TABLE 10
HIGH RATE RESULTS
ANSUL CHEMICAL COMPANY

Agent	Wt. of Agent Discharged, g	Wt. Effectiveness Relative to Halon 1301
Halon 1301	960	100
" 1211	1355	72
" 1011	1325	72
" 2402	1020	94
" 1202	1250	77

Such an explanation correlates the CAA data of Table 10 fairly well.

One of the common methods of evaluating agents in the past has been by a performance index which was the numerical product of the extinguishing time and the weight of the agent used. This resulted in a number with the usual units of pound seconds. The lower this number, the better the agent. This method of evaluation has no merit except near the optimum rate as can be seen by study of Figure 5. Any number of different performance indices can be calculated for one agent depending upon the application rate.

With a realization of the large effect of agent application rate, it is of interest to calculate these rates for reported fire tests. These rates were calculated for informative purposes only and represent average application rates. In a hand extinguisher, of course, the application rate decreases with discharge time since the propelling pressure decreases throughout discharge. In most cases the weight of agent used and the extinguishment time are given and these are used to calculate the rates. It is recognized that differences exist between extinguishment time and agent application time in many reported fire tests, but these differences are usually slight.

Malcolm^{4, 8, 9, 12} reports the following results from the ERDL study that led to adoption of Halon 1301 in the Army hand fire extinguisher:

TABLE 11

TUB FIRE TESTS
U. S. ARMY ERDL

Class B, 24 inch diameter tube fire. Agent pressurized with nitrogen to 400 psig. 60°F. tests.

Agent	Agent Used	Average Time Seconds	Wt. Effective- ness %	Rate lb./ sec.
Halon 1202	6.6	1.4	120	.295
" 1301	7.6	3.0	105	.158
" 1001	8.0	2.1	100	.238
" 1211	10.7	2.3	75	.290
" 2402	10.8	2.3	74	.294

Slightly different results were obtained with this same fire when the agents were pressurized to 800 psig. initial pressure.

Halon 1202	7.6	1.9	148	.250
" 1301	7.7	3.0	146	.161
" 2402	10.5	2	107	.327
" 1001	11.3	3.4	100	.208
" 1011	12.7	2.7	80	.295

The agents used are not exactly the same in both cases. Halon 1001 did not perform well at 800 psig which accounts for the high weight effectiveness of Halons 1301 and 1202 under these conditions. The conclusion to be drawn from the application rates that were used and a knowledge of the effect of application rate is that Halon 1301 was markedly superior to the other agents and that a rating based on weight effectiveness is not valid for these tests. Of course, since this work was of a screening nature, only a limited effort was made to optimize the mechanical equipment. Two and one-half-pound CO₂ extinguishers were simply charged with 2 pounds of agent, pressurized with nitrogen, and discharged. For this reason, these tests must be treated with caution. Other tests are reported on this same two-foot diameter tub fire which compare Halons 1301 and 1011. In this case, the application rates for the two agents were the same. The results may be summarized as follows:

TABLE 12

TUB FIRE TEST
U. S. ARMY ERDL

Agent	Application Rate Lbs/sec.	Wt. of Agent, Lbs.	Time to Exting- uish, Sec.	Nitrogen Pressure
Halon 1301	0.2	0.6	2.5	180 psig
Halon 1011	0.2	1.25	6	400 psig

(Essentially Underwriters Laboratories procedure 37, except conducted outdoors)

Some five gallon gasoline spill fires were also run with these two agents. The area was approximately three feet by twenty-five feet in size, and a 20-second preburn was allowed.

TABLE 13
FIVE-GALLON SPILL FIRES
U. S. ARMY ERDL

Agent	Extinguisher Type	Wt. of Agent Lbs.	Application Rate Lb./Sec.	Extinguishment Time, Sec.
Halon 1301	15 lb. CF ₃ Br	4.81	~ 0.5	8
Halon 1301	15 lb. CO ₂	7.375	~ 0.5	12.3
Halon 1011	15 lb. CF ₃ Br	14.125	~ 0.88	16.0

The above data introduce another variable, the agent application pattern. Approximately 50% longer extinguishment time was required for Halon 1301 discharged from a 15-pound CO₂ cylinder than from the 15-pound Halon 1301 cylinder. The results for Halon 1011 would doubtless also change if discharged using a more optimum pattern for this agent.

The large improvement that can be made in the effectiveness of an agent by concentrated development work is well illustrated by the program that led to the Army's new 2 3/4-pound Halon 1301 extinguisher. Results of some of the final fire tests after several model improvements were made are given in Table 14. Application rates were not given but were calculated from the weight of the expended agent and the extinguishment time. Again, these represent average rates over the whole discharge period. Study of Table 14 shows that this small unit affords a very large measure of fire protection.

TABLE 14
LARGE TUB FIRE TESTS
U. S. ARMY ERDL

Agent Halon 1301
Wind 4 mph. Temperature 76°F.
4 Foot Diameter Tub Fire

Model	Horn Dimensions Dia. x length, inches	Orifice Dia., Inches	Agent Used Oz.	Extinction Time, Sec.	Appli- cation Rate lb/sec.
T-3	1 7/8 x 2 3/4	0.128	41.5	14	0.185
T-3C	" " " "	"	38	32	0.074
T-4B	1 3/4 x 2 1/2	0.098	17	3.0	0.355
T-4B	" " " "	"	17.5	4	0.273
Wind 4 mph. Temperature 84°F. 4 Ft. x 4 Ft. Spill Fire					
T-3C	1 7/8 x 2 3/4	0.128	42	16.4	0.160
T-3C	" " " "	"	47.5	11.4	0.261
T-4B	1 3/4 x 2 1/2	0.098	32.5	8.6	0.236
T-4B	" " " "	"	30	7.4	0.253

Some additional ERDL work on the effect of orifice and horn size is of interest. The data are reproduced here in Table 15, because both Halon 1301 and 1202 were used. In this case a 4 foot x 4 foot spill fire containing three quarts of motor fuel was used. No preburn time was allowed. These test conditions apparently apply also to the spill fire reported in Table 13. Application rates were calculated and again represent averages over the total discharge period. These data show Halon 1202 to be very effective although application rates were higher for this agent than were obtained with Halon 1301 in most of the ERDL work.

TABLE 15

16 SQUARE FOOT SPILL FIRE TESTSU. S. ARMY ERDL

4 foot x 4 foot spill fire
 Agents pressurized to 400 psig. with N₂
 2 1/2 pound CO₂ cylinder

<u>Agent</u>	<u>Horn Dimensions</u> <u>Diameter x Length,</u> <u>(inches)</u>	<u>Orifice</u> <u>Diameter,</u> <u>(inches)</u>	<u>Agent</u> <u>Used,</u> <u>Oz.</u>	<u>Extinguishment</u> <u>Time, (Seconds)</u>	<u>Application</u> <u>Rate,</u> <u>(Lbs./Sec.)</u>	<u>Successful</u> <u>Extinguishment</u> <u>(No. of Trials)</u>
Halon 1301	1 13/16" x 5"	.0625	6.	2.7	.139	3/3
	Ditto	.0442	12.5	15.7	.050	2/3
	"	.0294	8.	13.6	.037	2/3
Halon 1202	"	.0625	9.7	2.4	.252	3/3
	"	.0442	8.7	2.6	.208	3/3
	"	.0284	5.7	5.3	.067	3/3
	1 13/16" x 2 1/2"	.0625	8.3	1.7	.305	3/3
	Ditto	.0442	5.3	1.8	.184	3/3
	"	.0284	3.3	3.3	.062	3/3
	1 13/16" to 3" dia. by 3 1/2"	.0625	11.3	2.6	.272	3/3
	Ditto	.0442	7.7	2.8	.172	3/3
	"	.0284	7.3	6.7	.068	3/3

Unfortunately, the bulk of reported fire tests have been performed using existing extinguishing equipment for agents of widely dissimilar physical properties. Halon 1011 because of its high boiling point is very sensitive to discharge pattern yet it is precisely because of this high boiling point that a variety of patterns can be obtained with this agent. The poorest pattern for this agent is a straight stream and yet this is a common pattern used with this agent. Also, in many of the fire tests described in the literature, the geometry of the agent discharge stream is not even qualitatively defined.

Another very important variable is the configuration of the fire. Everyone recognizes that there is no such thing as the best agent for all fires but it is also true that there is no best agent even for all Class B fires. Most investigators develop a "standard" fire and then investigate different extinguishing agents under more or less optimum conditions. The conclusions that are then drawn as to the relative merits of the agents studied are valid but only for fires similar in geometry to the one studied. The effect of the test fire is well illustrated in some work reported by the Bureau of Standards²³ on evaluating hand fire extinguishers of several types on ten fire configurations. The fires were primarily Class B but in some cases included Class A combustibles also.

Halon 104 and 1011 were the only vaporizing liquid agents included in this study but foam, dry chemical, and carbon dioxide units were also investigated.

Some recent work at Wright Air Development Center²⁷ on a simulated aircraft engine fire introduces a "critical saturation value" concept. This, briefly, is the minimum volumetric agent concentration required to extinguish the standard fire used. These values, which are based upon 100 per cent effective utilization of the agent were approximately:

Halon 1301	5.8 volume %
Halon 1011	4.0 " "

Insufficient data were obtained for Halon 1202 to determine the figure for this agent. These results are somewhat surprising in that most fire tests indicate a superiority of Halon 1301 over Halon 1011. Again, since the test fire was of unique configuration, caution must be exercised in attempting to transfer these results to other fires.

The Civil Aeronautics Administration ⁸ has also reported studies on simulated aircraft power plants using various agents. Whether the nacelle had exposed transverse stiffeners or a smooth lining had a large effect upon the amount of agent required to extinguish. High rate discharge systems were used in all cases and test results are described graphically in Figure 7. Notice that the effect of air flow through the compartment is detrimental up to a point and then is beneficial (in the case of exposed transverse stiffeners).

The general conclusions of the CAA were that Halons 1202, 1301, and 1001 were essentially equivalent and all very good agents with Halon 1011 having a slightly lower effectiveness.

Both explosion buret and practical fire test data are available on the effect of temperature upon agent effectiveness. The explosion buret data were obtained at the Purdue Research Foundation ⁴, 5, 8, 12. These data are reproduced in Table 16.

TABLE 16
EFFECT OF TEMPERATURE ON THE FLAMMABILITY PEAK
PURDUE RESEARCH FOUNDATION
ISOBUTANE (C₄H₁₀) AIR MIXTURES

Agent	Flammability Peaks (volume %)		
	-78°C.	+27°C.	+145°C.
Halon 1301	3.25	4.7	7.3
Halon 1001	3.75	6.75	8.3

As might be expected, the minimum concentration of agent necessary to render a fuel-air mixture non-flammable is directly proportional to the ambient temperature.

Some low temperature fire tests are reported by ERDL ⁴, 12 and may be summarized as in Table 17. Application rates were not given but were calculated using the extinguishing time and the weight of agent, which is subject to some error. All the experimental details were not given but the fire was in a 25 square-inch pan.

FIGURE 7
CAA Fire Extinguishing Test Results High Rate
Discharge System

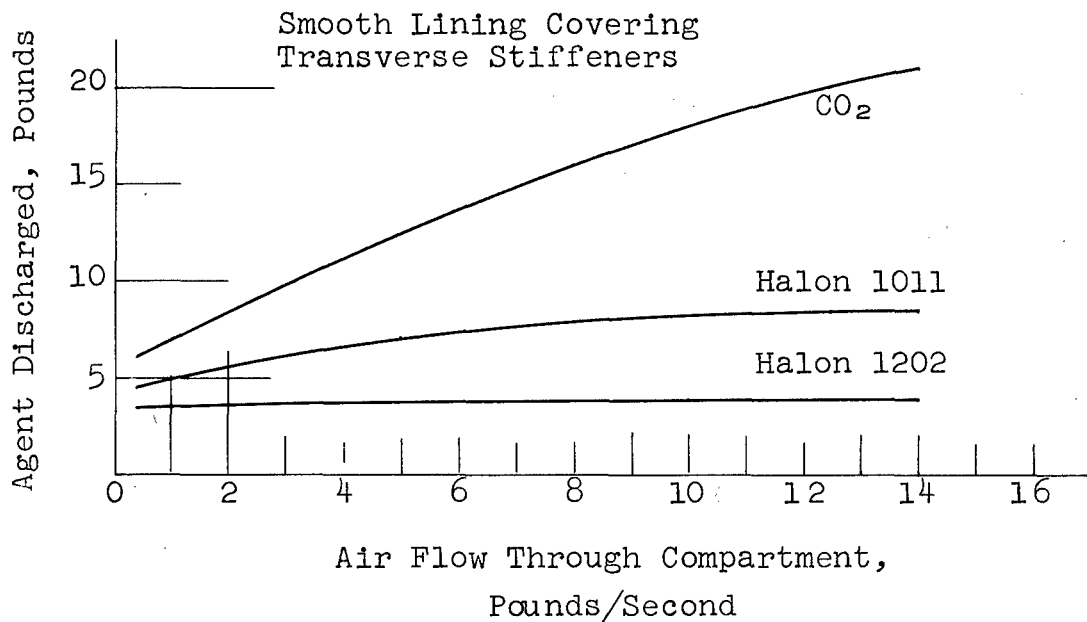
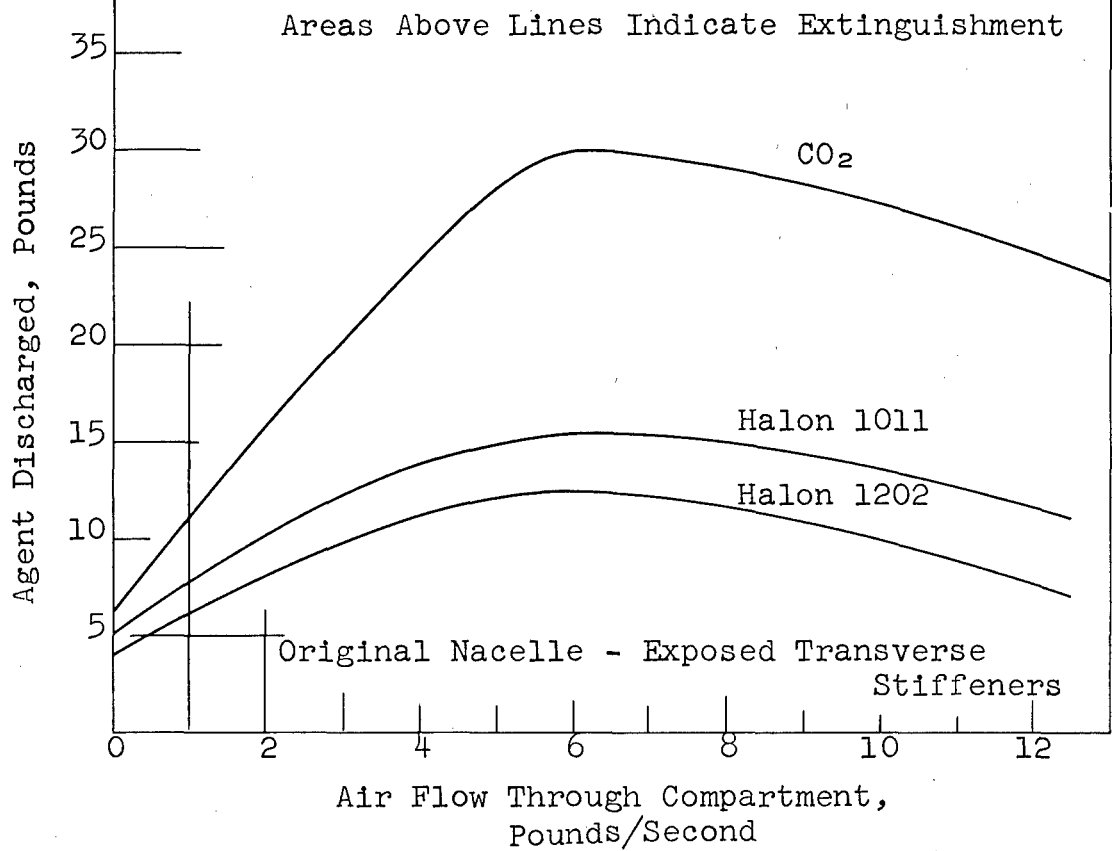


TABLE 17

LOW TEMPERATURE PAN FIRE TESTS
U. S. ARMY ERDL

MIST APPLICATION (PRESSURIZED TO 400 PSIG WITH N₂)

Agent	Exting- uishing Time, Sec.	Agent Wt. Oz.	Extinguish- ments Valid Tests	Temp. Range °F.	Appli- cation Rate, lb/sec.
1001	7.6	33.5	6/12	-56/-64	0.275
1202	6.6	24.5	11/11	-55/-65	0.232
1301	3.0	21.0	14/16	-50/-60	0.438
2402	5.5	24.0	3/10	-51/-58	0.272
Straight Stream Application (200 psig)					
1001	3.5	27.0	1/3	-56/-57	0.483
1202	4.0	26.0	1/1	-59/-60	0.406
2402	3.0	22.5	1/1	-54/-55	0.470

ERDL concluded that Halon 1301 showed a slight superiority over Halon 1202 at low temperature. In view of the much higher application rate of Halon 1301 in these tests this conclusion may not be valid.

2. Effectiveness Tests of This Study

A limited number of fire tests were run as a part of this study because it was apparent at the beginning that only two agents met Air Force requirement number 3, i.e., a toxicity approaching that of carbon dioxide. These two agents were Halons 1301 and 1211. The different fire configurations studied included square pans of various size, a 50 square-foot spill fire, the 50 square-foot spill fire containing a metallic obstruction, and a vertically spilling fuel fire. Pictures of these test setups are shown in Figures 18, 9, and 15.

All tests were run outdoors because a suitable indoor site was unavailable. As a result weather conditions (particularly wind) were uncontrollable variables. To minimize the effect of wind, tests were arbitrarily limited to days on which the wind velocity was below 10 miles per hour. The fact that winds of less than 2 mph exist only a small per cent of the time argues strongly against elimination of wind in practical fire tests. However, the presence of wind causes more erratic data in that wind can aid or hinder extinguishment. Tests were run using all five candidate agents on the square pan fires. The pans were 12 inches high and the lateral dimensions were such that a certain number of square feet

of fuel area were exposed. For example, the 10 square foot pan has inside dimensions of $\sqrt{10}$ or 3.17 feet. Four inches of water were placed in the pan along with two inches of fuel. The fuel used was a stove and lamp naphtha whose properties are given in Appendix IV, page 92. A 60-second preburn was allowed before extinguishment was attempted. This procedure is essentially the same as that used by Underwriters Laboratories in rating extinguishers except that the tests were run outdoors. 37

The agents were applied from a large cylinder (15 gallon capacity) that was equipped with a dip pipe and a separate inlet that allowed additional nitrogen pressurization during discharge of the agent. Since, in general, the amount of agent withdrawn was small in comparison to the volume of the cylinder, and the cylinder pressure remained constant during discharge, the agent application rate was uniform throughout the test. Agent flow was manually controlled by means of a 1/2-inch quick opening ball valve at the end of a flexible hose attached to the cylinder. Various orifices were incorporated in the discharge line downstream from the ball valve to obtain different flow rates. Different nozzle configurations were used to obtain fairly satisfactory discharge patterns for the five agents although by no means is it believed that the optimum patterns were achieved.

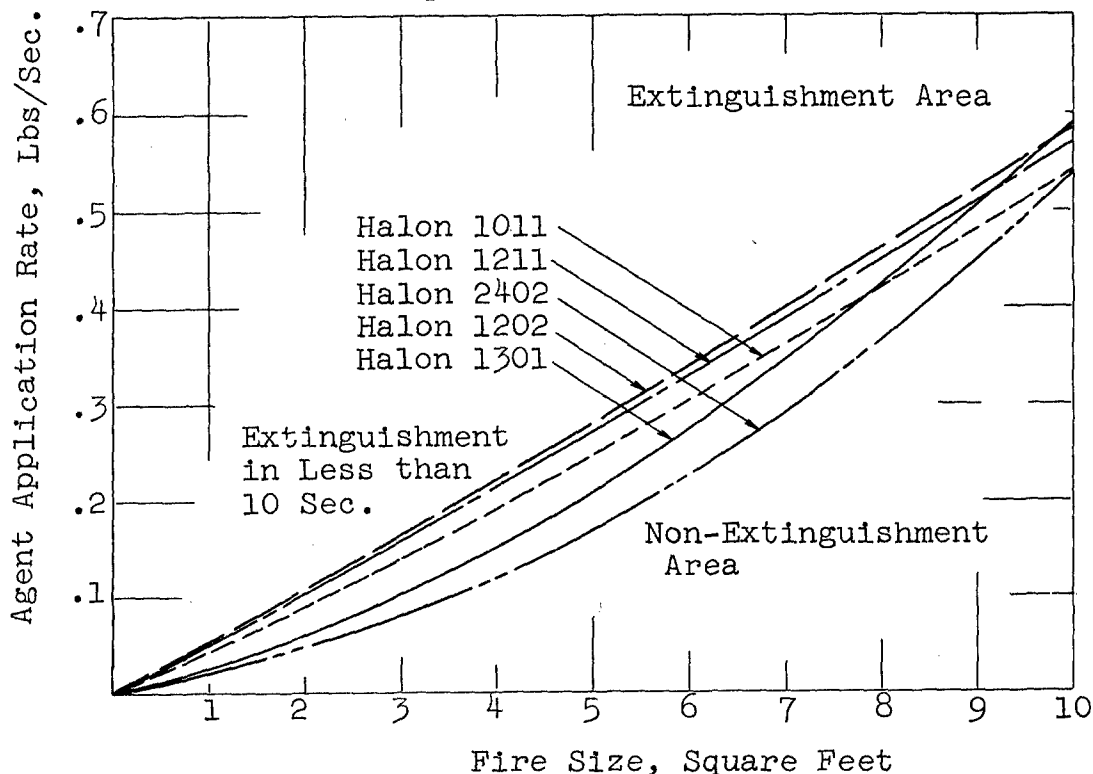
The human factor is present in all tests in that no mechanical apparatus was used to direct the agent stream on the fire. This also can lead to problems in that no two people will attack a fire in precisely the same manner. This human factor becomes a minor variable in the case of vaporizing liquids with suitable discharge patterns. It can be a major variable in using high boiling point liquids such as Halons 104 and 1011 that are discharged in a straight stream. In this case it is known that the proper technique is to spray the liquid against the far side of the fire pan and allow the resulting dispersed agent to fall back into the pan.

As a partial check on the effect of outdoor conditions and relatively inexperienced operators, several fire tests were made early in the study using commercial units that had been rated at 2 BC. Since a factor of 2.5 is used by Underwriters Laboratories to allow for the lack of skill by an average user, these extinguishers should extinguish a five square foot pan fire when used properly. Three types of extinguishers were used, Halon 1011, dry chemical and carbon dioxide. Halon 1011 and dry chemical dependably extinguished the five square foot fire but in no case was the carbon dioxide unit successful.

The data summarizing the valid pan fire tests for the five candidate agents are given in Appendix V, pages 93 through 99. The results are also presented graphically in Figure 8 which is a composite curve showing relative effectiveness as determined on these fires.

FIGURE 8

Fire Size Versus Agent Application Rate
Square Pan Fires



The test procedure can be described as follows:

Four inches of water and two inches of fuel are placed in the pan.

The fuel is ignited and a 60-second preburn is allowed.

The fire is attacked by the operator while two observers with stop watches obtain the extinguishment time and the agent application time. Normally, the application time was somewhat longer than the extinguishment time because of human reflexes.

The cylinder plus hose, nozzle, and valve are weighed before and after the test to determine the amount of agent used.

Figures 9, 10, and 11 show a typical pan fire test.

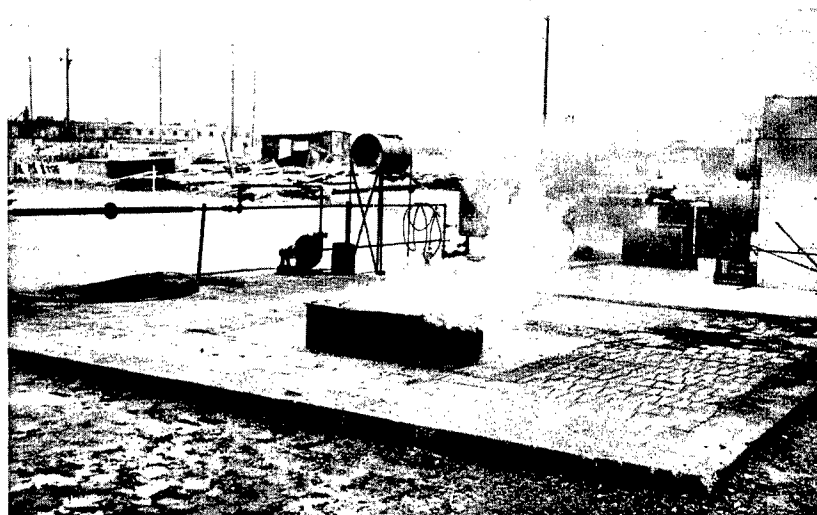


FIGURE 9
10 Square Foot Pan Fire
Test 06119-4
30 Seconds Have Elapsed
Of 60 Second Preburn



FIGURE 10
Test 06119-4
Agent - Halon 1211
Application Rate - 1.25 lb/sec.
U. S. Army 50 lb. Halon
1301 Nozzle - Modified



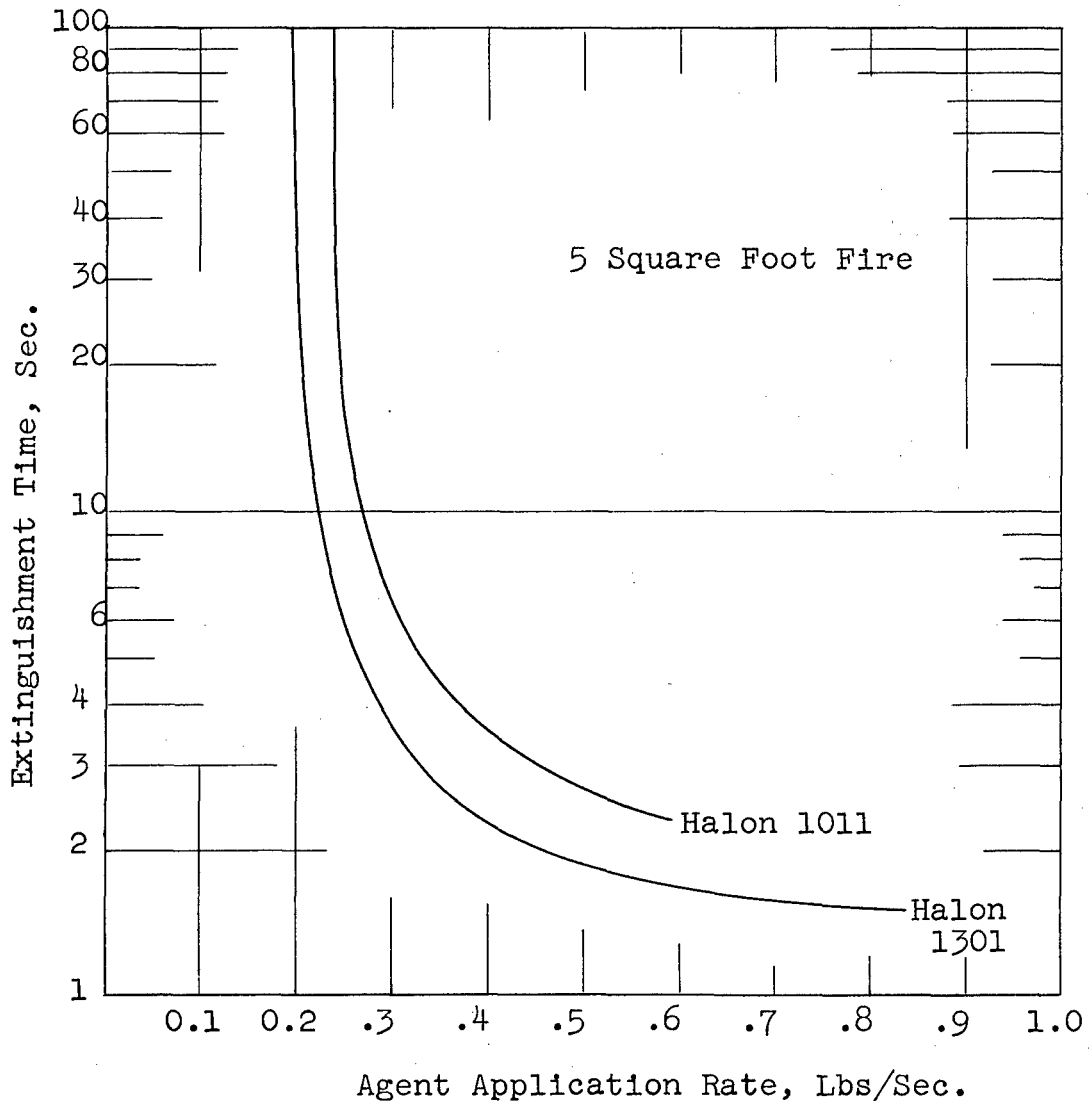
FIGURE 11
Test 06119-4

Extinguishment Time - 3.3 Sec.
Application Time - 3.5 Sec.

The agent application rate was determined by the amount used and the application time. The amount actually used in extinguishing the fire was, of course, somewhat less than the recorded amount because of the time lag before the agent could be shut off.

The usual procedure was to extinguish a given size fire using a given application rate of the agent. Lower and lower rates were then used until extinguishment became borderline and finally impossible. When this is done for several different fire sizes a plot can be constructed showing the "positive extinguishment area" and the "failure to extinguish area" as functions of the application rate and the fire size. If all variables were completely controllable, the areas of extinguishment and non-extinguishment should be separated by a narrow region, the width of which corresponds to a rapid increase of extinguishment time as the minimum application rate is reached. Figure 8 does not show extinguishment time as a variable but Figure 12 shows the effect of application rate on the extinguishment time for Halons 1011 and 1301 for the five square foot fire. Insufficient runs were made to satisfactorily determine these curves for all five agents and all fire sizes studied.

FIGURE 12



There are several methods of comparing effectiveness of these agents based upon pan tests. One would be to set a maximum extinguishment time and determine the necessary application rate to extinguish a given size fire within this time. This is essentially the method used by manufacturers of hand fire extinguishers. An extinguishing unit is required to have a minimum discharge life of ten seconds by Factory Mutual Laboratories and eight seconds by the Underwriters Laboratories. So the extinguishing unit is designed, incorporating the minimum amount of agent that can be discharged over an eight or ten second time interval, to extinguish a definite fire size.

Another method of evaluating agents is to compare the extinguishment times obtained by the agents at comparable application rates on a certain size fire. This method then results in a weight effectiveness rating inasmuch as the weight used is a product of the application rate and the extinguishment time.

The method used by Ansul ²² was based upon the minimum amount of agent at the optimum application rate that would extinguish the test fire. This method also results in a weight effectiveness rating.

A fourth method of evaluating agents by the numerical product of the weight of agent used and the extinguishment time is without merit, as has been discussed earlier. No method of evaluation will satisfy all objections but, in general, all methods except the fourth give similar results.

Figure 8 drawn with a maximum allowed extinguishment time of ten seconds. Successful extinguishments were made at rates lower than shown but the times were excessively long. This was particularly true for Halon 1011 which is not as rapid in its action as the other agents in the study. Halon 1011 gradually lowers the intensity of the fire until it finally extinguishes it. At the other end of the boiling point scale, Halon 1301 usually extinguished the fire quickly or not at all. However, when reflashing occurred, some long extinguishing times were experienced also with Halon 1301.

It should be pointed out that Figure 8 is only a method of presenting the data and does not describe the whole effectiveness picture. Only a limited number of pan tests were performed in this study and these were run in order to obtain an understanding of the general behavior of the agents and get some idea of effective discharge patterns. Only those tests considered valid are reported. A number of others were eliminated, primarily because the agent application patterns were not good. Halons 1011 and 2402, for example, are not effective in a straight stream on pan fires and good results with these agents were not obtained until interrupting screens were placed in the discharge nozzle. Halons 1211 and 1301 required discharge horns to obtain good results. Halon 1202 was the least sensitive to application hardware.

Also, an idea of the relative effectiveness of the candidates was necessary. While Halons 1011, 1301, 1202 and 2402 had received considerable attention by other investigators, this was not true of Halon 1211, and only a limited amount of information was found on this agent.

Actually, pan fires do not simulate the hostile fires for which the secondary agent on a crash truck is intended. The usual method of attack of a major crash fire is with mechanical protein foam. After the initial foam blanket is laid the secondary agent (presently Halon 1011) is used to extinguish the remaining fires which because of their geometry were not successfully covered by the foam. For this reason, three other type fires were studied at the suggestion of WADC. The first was a 50 square-foot spill fire, the second was the 50 square-foot fire containing a simulated wing section, and the third was a vertical spilling fuel fire. Figures 13 through 19 show the three types.



FIGURE 13
50 Square Foot Spill Fire
15 Gallons Fuel
10 Seconds Have Elapsed
Of 20 Second Preburn
Test 06119-1

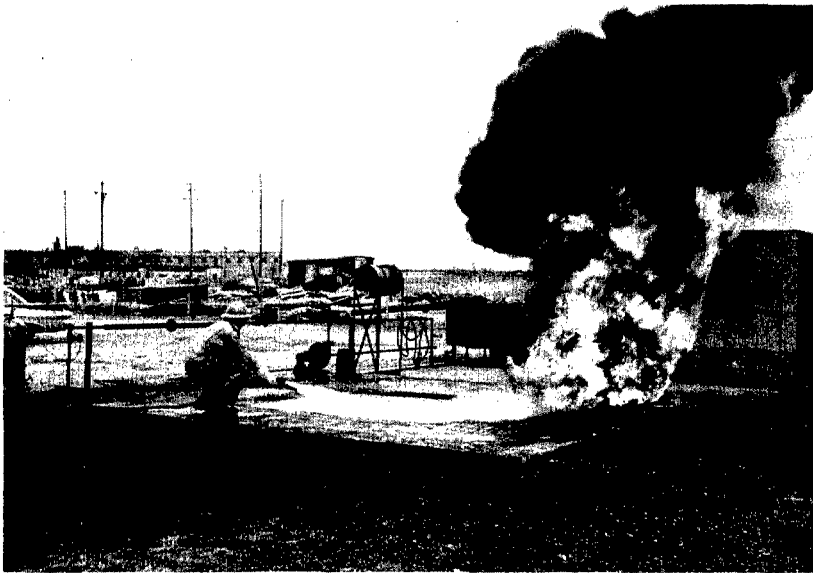
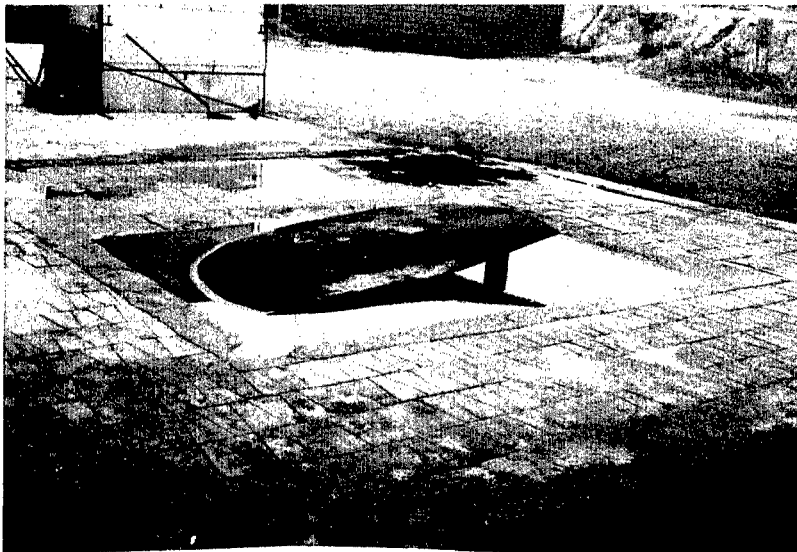


FIGURE 14

Test 06119-1
 Agent Halon 1211
 Application Rate - 1.3 lb/Sec.
 Extinguishment Time - 5.5 Sec.



• FIGURE 15

Simulated Wing Section in
 50 Square Foot Depression
 15 Gallons Fuel
 Test 06119-2

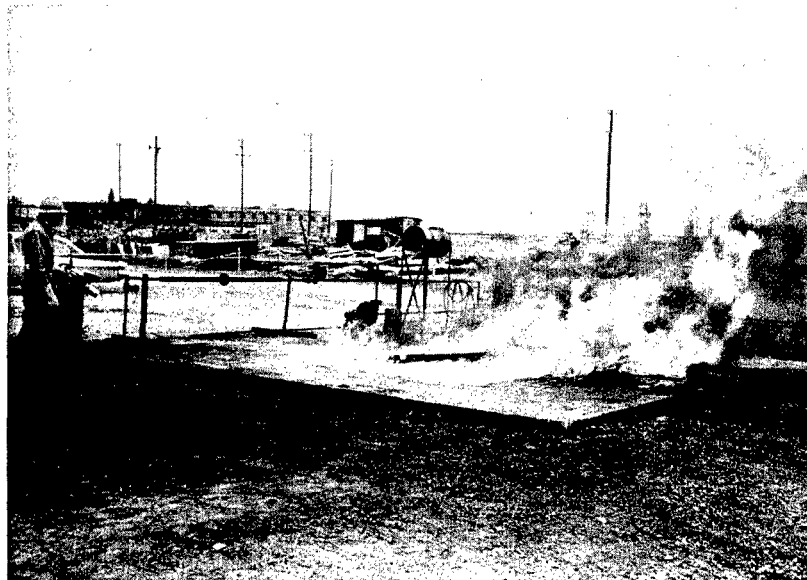


FIGURE 16
Test 06119-2
10 Seconds Have Elapsed
Of 20 Second Preburn

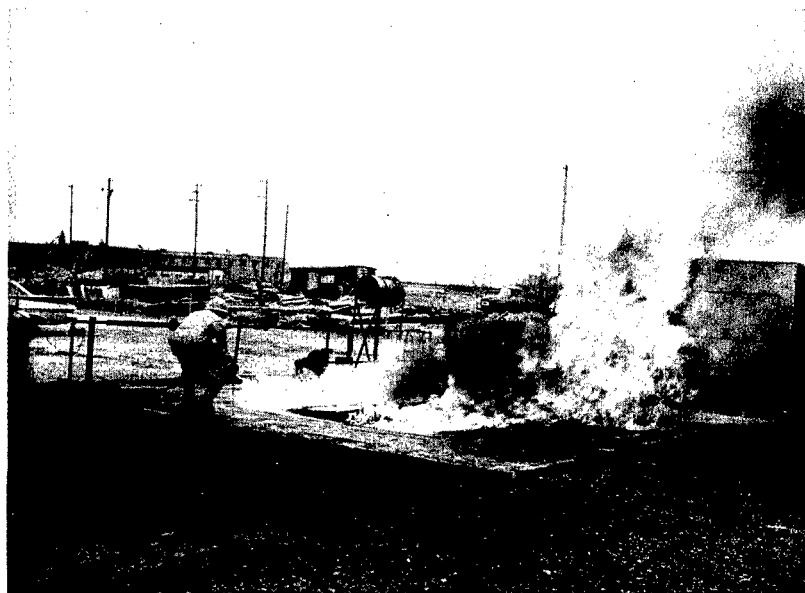


FIGURE 17
Test 06119-2
Agent - Halon 1211
Application Rate - 1.15 lb/Sec.
Extinguishment Time - 6.3 Sec.

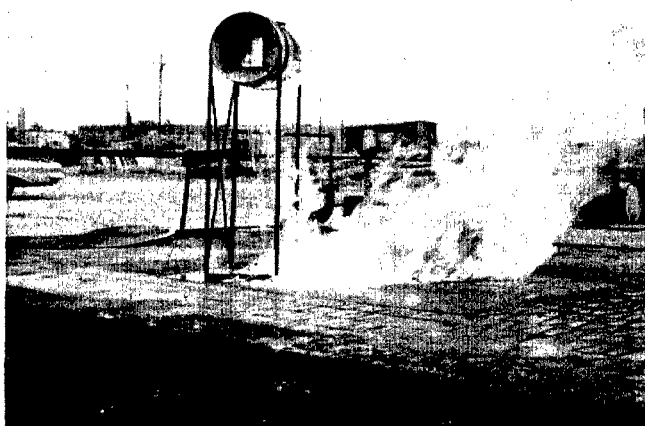


FIGURE 18
Spilling Fuel Fire
5 Gallons Fuel
Test 06119-3
10 Seconds Have
Elapsed of 20 Second
Preburn

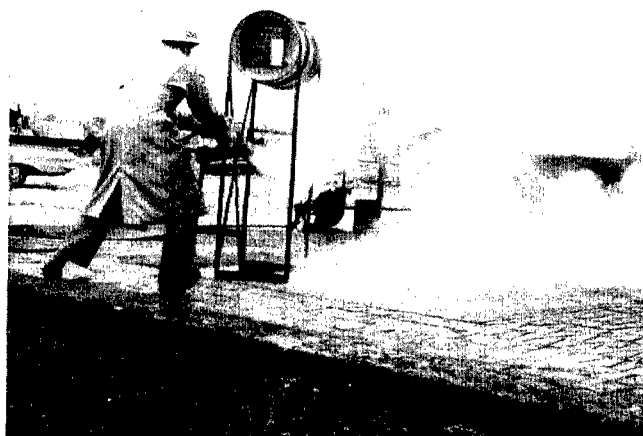


FIGURE 19
Test 06119-3
Agent - Halon 1211
Application Rate - 1.3 lb/Sec.
Extinguishment Time - 6.3 Sec.
Note how Ground Fire has Been
Reduced in Intensity

The experimental procedure on the 50 square-foot spill fire (6 feet 3 inches by 8 feet) was first to wet down the area with water to fill depressions so that the fuel would completely cover 50 square feet. Fifteen gallons of fuel were then added which corresponds to 0.3 gallons per square foot or an average depth of about 1/2 inch. A 20 second preburn was permitted on these fires before extinguishment was attempted.

By the time these larger fires were studied Halons 1202 and 2402 had been eliminated, primarily on the basis of toxicity, and only Halons 1301, 1211 and 1011 were included. Halon 1011 was retained for comparative purposes throughout since it is the agent now used.

It was on these larger fires that the "reflash" problem was expected and experienced, although this same phenomena was also found in the 10 square-foot pan fires. A reflash or flash back is the insidious reignition of a fuel area that has previously been extinguished. This reignition is surprisingly rapid and the flame reaches maximum intensity in a very short time in contrast to the original ignition of the fuel. In the latter case, maximum intensity does not seem to be reached until about 10 to 15 seconds of burning have occurred. This rapid increase in intensity upon reflash is due to the fact that the fuel is boiling at the end of the allotted preburn time. Only a few seconds are required to sweep the 50 square-foot area clear of flames but the vapors continue burning downwind from this area. In these few seconds the fuel does not cool appreciably and continues to generate large amounts of vapor which feed this downwind flame. A small flicker of flame which usually feeds back along the side of the extinguishing agent stream is then able to reignite the 50 square-foot area very rapidly.

It is apparent that the reflash problem on large fires can be very dangerous to fire fighting personnel. Usually, hostile fires have complicated geometry with various metallic obstructions present. These obstructions can act as flame holders and reignition sources, thus increasing the danger of reflash.

The results of the 50 square-foot fires are given in tabular form in Appendix V, page 100. The reflash problem was experienced for all three agents (Halon 1011, 1301 and 1211) whenever the agent application rate was lowered to a borderline value. However, at approximately equal application rates (slightly over 1 lb./sec.) Halon 1301 was troubled by reflash when Halons 1211 and 1011 were not. This is believed due to the fact that the

boiling point of Halon 1301 is so low (-72°F.) that no agent enters the fuel in the liquid phase. Drops of liquid can be observed falling into the fuel with Halons 1211 and 1011.

Work by other investigators indicates that large amounts of chemical agents must be added to the fuel in the liquid phase in order to render the fuel inert to combustion. These amounts are surprisingly large so this cannot be the explanation for the fact that reflash was less of a problem for the higher boiling point agents. What probably occurs is that the agent droplets that fall into the hot fuel revaporize and an area above the fuel surface is rendered non-flammable for a short interval of time. Since initiation of combustion occurs in the vapor state this has the effect of inerting the fuel. However, inerting effect is of only short duration.

The simulated wing test fire consisted of a 6 foot by 4 foot by $1/4$ inch sheet of steel supported on one end by a brick. The sheet was set in the 50 square-foot depressed area. Fifteen gallons of fuel were added and a 20 second preburn was again allowed. Pictures of this fire are shown in Figures 15, 16, and 17 and the results of these tests are given in Appendix V, page 102.

In general, when using the same agent application rates, the simulated wing fire was more difficult to extinguish than the 50 square-foot fire. This particular fire configuration is only one of an infinite number that could have been used. It should be obvious that wind direction could be an important variable in this one fire situation (the wind in these tests blew from the low to the supported end of the plate). So again, caution should be exercised in attempting to transfer results from this one unique fire geometry to others.

The last type of fire studied was a spilling fuel fire, pictures of which are shown in Figures 18 and 19. The test procedure was to quickly dump five gallons of fuel into the 30-gallon drum supported six feet above the ground. The fuel drained out of twelve $1/4$ " diameter holes drilled into the bottom of the drum and onto the ground. A 20 second preburn was allowed. In no case had all the fuel drained out of the 30-gallon drum when extinguishment was secured. This was a particularly difficult fire to extinguish because there were essentially three fires; on the ground, in the drum, and the draining fuel itself. In addition, some of the fuel would wet the supporting angle iron legs which would then act as flame holders. The successful technique was to first

extinguish the ground fire and in so doing inert that fuel for a few seconds. Then the nozzle could be switched to the drum which was readily extinguished, and finally to the spilling fuel. Figure 19 shows the operator beginning the attack on the spilling fuel after extinguishing the fire inside the drum. The fuel on the ground has not reignited after its original extinguishment. Results of tests on this fire are given in Appendix V, page 103.

It would be desirable to say that one of the five candidate agents is the most effective under all conditions. This is not possible since the relative effectiveness of these agents depends upon the fire geometry to such a large extent. The test fire can be constructed to penalize or to favor any agent without realization that this is being done. It is no more or no less valid to introduce the agent from a nozzle inside a fire pan than it is to set a minimum distance that the agent must transverse to reach the fire. Both techniques have been used but it is obvious that the former method may penalize the higher boiling point agents and the latter may penalize the lower boiling point agents.

Some general remarks can be made about relative effectiveness, however. First of all, it may be concluded that laboratory studies conducted in an explosion buret do not correlate well with actual fire tests. Secondly, at comparable application rates, Halons 1301, 1202, 2402 and 1211 will usually extinguish a fire faster than Halon 1011 and therefore with less expenditure of agent. Thirdly, Halon 1301 does not rank as well on the larger fires because it gives a more serious reflash problem although it is the most effective agent on the pan fires. Halons 1202 and 2402 rank as well as 1301 on pan fires. They were not evaluated on the larger fires, although they would presumably be very good, since the reflash problem should be minor with these agents. Halon 1211 was not quite as effective on pan fires as Halons 1301, 1202, and 2402 but surpassed Halon 1301 in the 50 square-foot fire.

Since optimum dispersing equipment for all the different application rates was not available any intensive development work should markedly improve the effectiveness of all five of the agents. This type of development is not usually possible in any evaluation program but follows choice of an agent and the application area.

C. Comparative Toxicity of Agents

1. Past Experience with Vaporizing Liquid Extinguishers

It is evident that the use of any fire extinguishing agent is a compromise between the hazards of the fire, smoke, fumes, and a possible increase in hazard due to the toxicity of the extinguishing agent used. The problem resolves itself into selecting the fire extinguishing agent which reduces the total hazard the most. This consists of using the least toxic agent which is effective for the particular type of fire, keeping in perspective the toxic nature of the fire itself. The effectiveness, stability and physical properties of the various extinguishing agents are discussed in other sections of this report. This section will consider only the current Air Force requirement regarding toxicity.

The use of vaporizing liquids in fire extinguishers has long been of concern due to the toxic nature of some of the materials which have been and which are being used. The high toxicity of methyl bromide, for example, is well established and it has not been used in recent years where human contact is likely. The use of carbon tetrachloride (Halon 104) has also been seriously questioned. It must be concluded that much of the concern is unwarranted since a search of the literature indicates that the actual number of deaths due to the use of carbon tetrachloride in extinguishing fires is exceedingly small³⁵, particularly when one considers the widespread usage of this material since the early 1920's. Unfortunately, the hazards associated with carbon tetrachloride have in many cases, been the subject of emotional outbursts rather than rational thinking. This adverse publicity has resulted partially from the fact that the cases where no injury has resulted or where lives have been spared have not made the headlines. The actual documented cases of deaths due to carbon tetrachloride are only rarely related to extinguishing fires and if associated with a fire, quite often are the result of improper use in confined areas or failure to leave an area after the fire is out. The decomposition products of carbon tetrachloride, particularly phosgene, are often blamed for causing injury but when a thorough study of the literature is made, it is obvious that it is the toxicity of the agent per se and not the decomposition products which are responsible. Carbon tetrachloride has been shown to breakdown thermally to hydrochloric acid with small amounts of phosgene also being formed^{67, 68}. Yet, the symptoms described

from injury in a fire and the delay in their occurrence is evidence that the injury is due primarily to carbon tetrachloride itself and not to hydrogen chloride or phosgene. This has recently been pointed out by Fawcett ³⁵ for carbon tetrachloride and by British workers ⁶⁴ for bromochloromethane. Other workers have indicated that the decomposition products of carbon tetrachloride are extremely painful to inhale and hence a person will not willfully tolerate exposure if escape is not blocked ^{53, 61, 67, 69}. However, since escape can be blocked, particularly in military applications, less toxic fire extinguishing agents have been sought.

The problem, then, is somewhat simplified for the toxicologist because any compound, which shows a reasonable improvement over carbon tetrachloride (2 to 3 fold or more), should present slight hazard unless flagrantly misused. Halon 1011 (Bromochloromethane) has been considered as such a replacement. However, it has met with disfavor for several reasons, not one of which, in itself, is serious enough to eliminate Halon 1011 from consideration. No reports of deaths or injury due to Halon 1011 in fighting fires are found in the literature. This is probably due in part to the low capacity of this compound to produce liver injury. Unfortunately, the low hepato-toxicity, in comparison with carbon tetrachloride, was not taken into account in the very cursory study by the Underwriters Laboratory ⁶¹ which placed carbon tetrachloride and Halon 1011 in the same grouping on the basis of toxicity. This classification by Underwriters has probably been the main deterrent to the substitution of Halon 1011 for carbon tetrachloride since this agent is admittedly more effective than carbon tetrachloride in extinguishing test fires.

Another block to the acceptance of Halon 1011 has been the discomfort it causes when spilled on the skin or in the eyes. While this effect is certainly not hazardous to health it causes considerable concern to firemen exposed to it and has, as a result, discouraged them from using Halon 1011 to the point of complete refusal in some instances.

2. Selection of Criteria for Comparing Toxicity

In the selection of new and better fire extinguishing agents, it is necessary that the toxicologist examine them and evaluate the potential hazards to health of each candidate and compare each with existing agents. The acute and chronic toxicity, when inhaled,

the effects resulting from skin and eye contact, and the toxicity of the pyrolyzed vapors must be considered.

a. Toxicity Resulting from Thermal Decomposition

As is shown in the section on thermal stability, the past studies on the toxicity of the products of thermal decomposition have been primarily measures of thermal stability under one particular set of conditions. Since the decomposition products are somewhat the same for all the compounds studied, it is probably more valid to use thermal stability as a criterion than it is to set up an animal experiment in which animals are exposed to the vapors which have been artificially decomposed. It is interesting to note that after conducting fire tests under practical conditions ⁶⁴, British investigators concluded that the laboratory type studies in heated tubes are probably much too severe to be practical and they recommend primary consideration of the toxicity of the agent itself. It is also of interest that many of the laboratory tests have been designed to produce a maximum of smoke and fumes rather than being based on efficient use of the extinguishing agent ^{52, 61, 69}. It is unfortunate that the workers conducting these experiments have eliminated from their thinking the hazard of fire and the toxic nature of the resulting smoke and fumes. As a result the toxicity problem of the extinguishing agent has been placed somewhat out of perspective. For example, the mortality shown for the unaltered vapors by the Army Chemical Center ⁵² is not above the mortality that could be normally expected from no exposure for a group of this size (20 mice and 40 rats). For the thermally decomposed vapors, the increase in mortality is probably significant only for carbon tetrachloride and Halon 1202. Also, in the investigation of the toxic products resulting from rapid extinguishment of the test fire, it should be noted that the following quantities of agents were used:

Halon 1301	0.3 lbs.
Halon 1202	0.9 lbs.
Halon 1011	1.3 lbs.
Halon 104	2.6 lbs.

While it is valid to use less of the more effective agents in evaluating the toxicity hazard, no practical fire tests indicate such a difference in effectiveness as to justify the large differences in the amount of agents used. To this extent the results favor Halon 1301 and penalize Halons 1011 and 1202 unfairly. It seems logical, on the basis of past experience and the data

presented in the other sections of this report, to base the comparison of toxicity on the unpyrolyzed vapors only and to consider thermal stability or the extent of decomposition as the measure of the health hazard presented by pyrolysis.

b. Chronic Vapor Toxicity

Chronic vapor toxicity, that resulting from frequently repeated exposures over long periods of time, is of little importance to the ultimate user of fire fighting equipment. It may be of concern to manufacturers and persons filling extinguishers and handling the agent on a routine basis. The hazards of chronic exposure to any material can always be overcome by proper engineering, and do not present an insurmountable obstacle in any case.

c. Effects of the Agent on the Skin and Eyes

Also of slight concern is the toxicity resulting from absorption of the chemical through the skin. Despite the stinging and burning which some agents cause when in contact with the skin and eye, the volatile nature of the compounds under consideration, the short duration of contact with the skin, and the available toxicological data makes this route of contact of minor importance to the user of these agents in extinguishing fires. The low boiling point of Halon 1301 (-72°F.) makes freezing of the skin and eyes a possibility, however.

d. Acute Vapor Toxicity

(1) General Considerations

The prime concern of a fire extinguishing fluid is the toxicity resulting from inhalation for short periods of time of concentrations of vapor in the range likely to be encountered in extinguishing a fire, or when accidental discharge of an extinguisher occurs. Ideally such concentrations should not be capable of causing death or serious organic injury, or impairing equilibrium, coordination or judgment. The vapor toxicity of a chemical is most conveniently determined by exposing small laboratory animals to known concentrations for various intervals of time and observing the effect upon the animals. The use of small laboratory animals is, of course, subject to the biological variation between animals of the same species and also to the differences in responses between species.

The use of groups of animals of a reasonable number is necessary to minimize the error which could result from interpretation based on data obtained on one or two animals, as has often been the case in data published to date 56, 61, 69. The use of two species helps to lessen the probability of an unusual susceptibility or resistance to a particular compound by any one species.

To satisfy the limitations listed above, the experiments described herein were conducted on two species, rats and guinea pigs. To limit variation between individuals, animals were selected from young adults of a suitable weight range and from a homogeneous stock. Generally, groups of eight to ten animals were exposed to each particular set of conditions in order to get large enough groups to rule out individual variation.

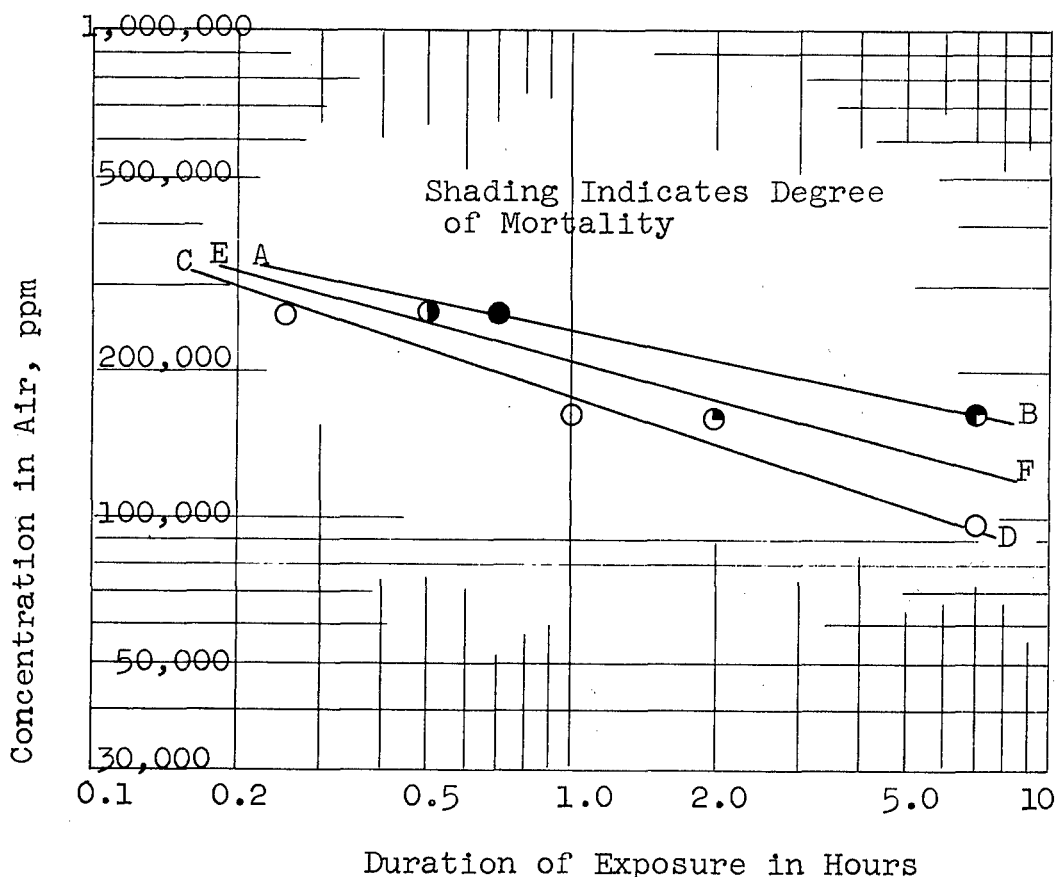
(2) Comparison of Data

It is dangerous to compare the data obtained on vapor exposures to two or more compounds if the data are limited to the response at one prescribed set of conditions. Slight variations in response often make comparison at one particular concentration or one particular duration of exposure misleading. It is much more desirable to be able to "average" the results of several different time intervals at several different concentrations, and therefore have a broader basis for comparison. Such a comparison is extremely difficult to do in tabular form since the effect on any particular group of animals is a function of both the concentration and the length of time to which the animals are exposed to that concentration. It is always necessary to consider all exposures in terms of concentration and time. This concentration-time relationship is easily expressed graphically on log-log coordinates. Using Figure 20 as an example, concentrations are plotted on the vertical scale and duration of exposure on the horizontal. After several exposures of different duration have been made at a particular concentration and the mortality determined, it is possible to record this data on the graphs by suitable symbols. For example, in Figure 20, solid circles are used to represent exposures causing all animals to die and open circles are used to represent the exposure intensities which caused no mortality. After this has been done for three or more different concentrations, it is generally possible to connect by a straight line these points representing an equal percentage of mortality. Three such lines are of importance in expressing mortality data obtained from vapor exposures. In Figure 20 line AB represents

the minimum intensity of exposure causing death to essentially all animals treated. This is sometimes referred to as the LCT 100, the lethal concentration-time for essentially 100% of the animals. The second line, CD, represents the maximum intensity of exposures causing essentially no deaths in animals exposed. This is sometimes referred to as LCT 0. The third line EF represents the graphically derived conditions expected to cause death to half of the animals exposed. This is sometimes called the LCT 50, the conditions of exposure (concentration and time) expected to cause 50% mortality. While the determination of the 100% and 50% lethal conditions is of importance in animal experiments, it is obvious that exposures to humans should ideally be limited to those causing no deaths. The exposure conditions causing essentially no deaths to animals, line CD, were therefore selected as the most practical criteria by which to compare the candidate extinguishing agents. The use of this criterion is further strengthened by the observation that the compounds studied were generally lethal as a result of their

FIGURE 20

Summary of Single Vapor Exposures of
Male Rats to Halon 1211 (CBrClF_2)



anesthetic effects and the animals that were removed from the exposure before death generally quickly and completely recovered and did not show significant injury of the internal organs. Had appreciable organic injury resulted it would have been desirable to determine a fourth line representing the exposures causing no detectable gross or microscopic injury. Such a study which involves large groups of animals and extensive histopathological work was beyond the scope of this project.

The use of the LCT 0 must not be the sole criteria, however, since impairment of equilibrium and judgment are also of major importance. Hence, observations of the degree of anesthesia or other effects upon the central nervous system resulting from the various exposures were also recorded, as well as other clinical signs and gross pathological changes pertinent to the exposures.

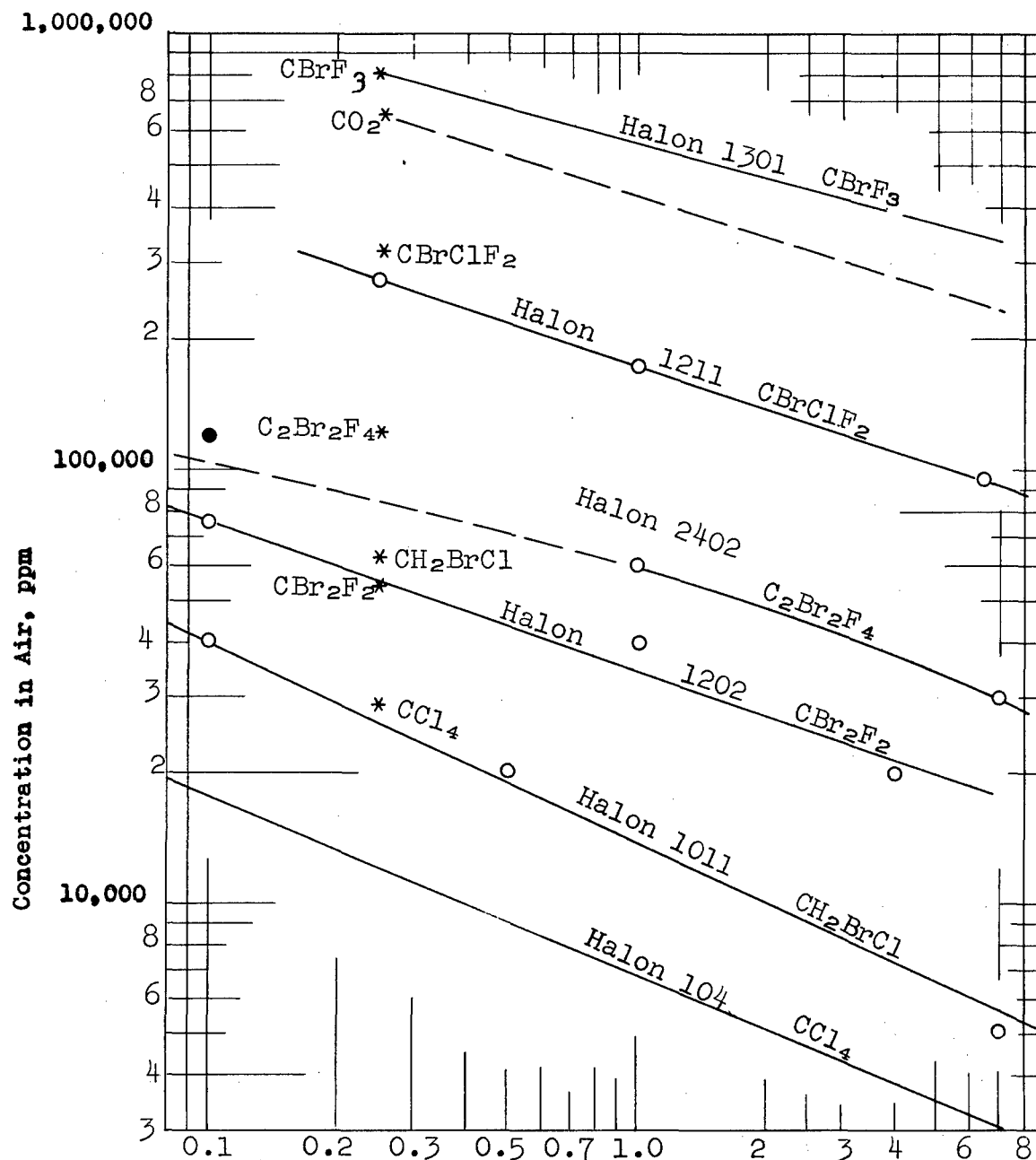
Because of innate limitations of vapor exposure equipment, a six minute exposure was considered as the minimum which could be administered reproducibly.

The acute vapor toxicity results obtained with rats and guinea pigs are presented in the graphical form described in Figures 21 and 22. The toxicity data appear in Appendix VI, page 104 and a detailed description of the experimental method used appears in Appendix VII, page 115.

(3) High Concentrations and Anoxia

Because of the extremely low toxicity of some of the agents under consideration it was necessary to establish a practical upper limit of concentration to be studied. This is generally considered to be about 30% by volume for long exposures, since higher concentrations result in anoxia due to displacement of oxygen. For example, a concentration of 30% of any gas in air results in 14% oxygen; 50% of any gas, 10% oxygen. At levels of 10% oxygen or less, human experience has shown that unconsciousness and death can result in a matter of minutes and it appears proper to consider 50% as a maximum level of any so-called inert gas for short exposures. Although the high (50 to 80% for 15 minute exposure) approximate lethal concentrations (ALC) reported by the Army Chemical Center ⁵⁶ are valid for rats they are not valid for humans. The ALC of even a totally inert gas should not exceed 50% for short exposures in the case of humans, and it seems prudent to reconsider the published ALC's on this basis.

FIGURE 21
Comparison of Acute Vapor Toxicity of Candidate Agents
Single Exposure Causing Essentially No Mortality
to Rats



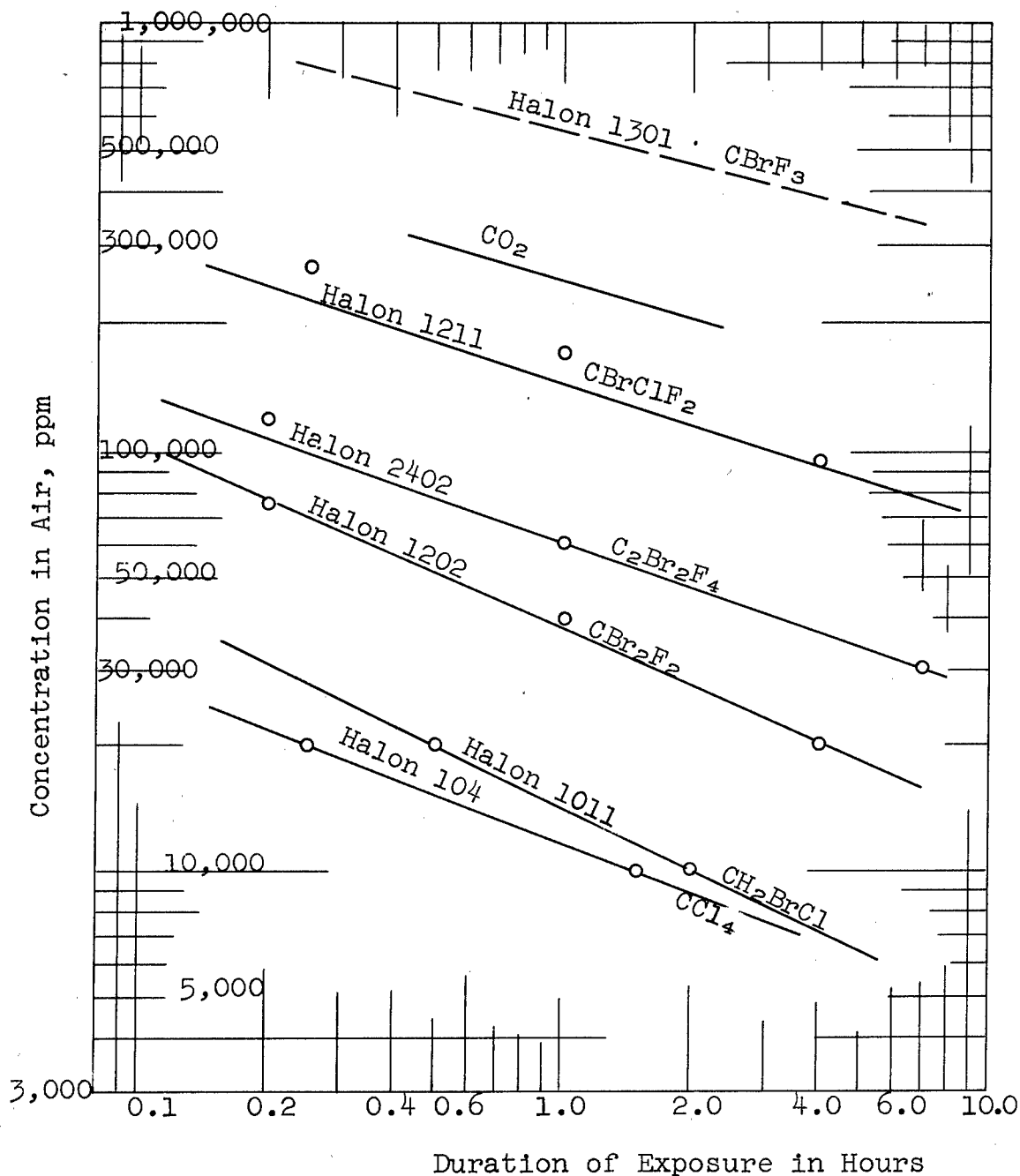
* Army Chemical Center ⁵⁶ Approximate Lethal Concentration (ALC)

CO_2 line is postulated on the basis of the ALC.

Line for Halon 1301 is based on ALC and data presented by Treon, et al.⁵³.

FIGURE 22

Comparison of Acute Vapor Toxicity of Candidate Agents
Single Exposures Causing Essentially No Mortality
(LCT 0) to Guinea Pigs



The line for CO₂ is based on 3 Animals per Group
(Underwriters Laboratories)

Line CBrF₃ is a best estimate based on available data.

The Army Chemical Center ⁵⁶ did the original toxicity work on various extinguishing agents that showed promise as a result of the Purdue Research Foundation study 5. These were range finding studies with only one animal used per exposure and the exposure time in all tests was fifteen minutes. The approximate lethal concentrations (ALC) reported are somewhat comparable to the maximum concentrations causing essentially no mortality LCT 0 given in the present report. For the five agents of this study (plus carbon tetrachloride for comparison) the results obtained by the Army may be summarized as in Table 18.

TABLE 18
APPROXIMATE LETHAL CONCENTRATION (ALC)
15 MINUTE EXPOSURE
ARMY CHEMICAL CENTER

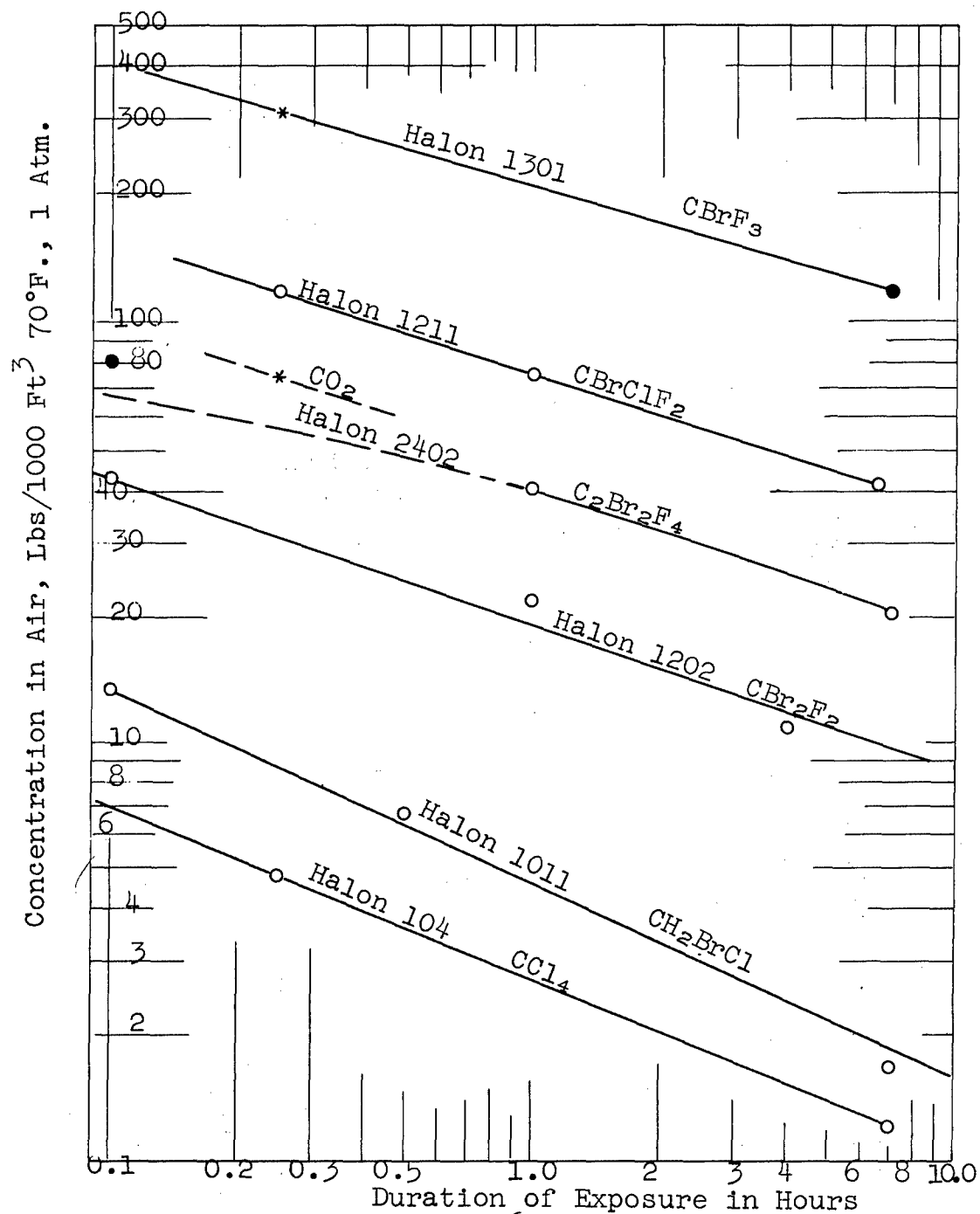
Agent	Undecomposed Vapor		Pyrolized at 800°C.	
	mg/l	ppm	mg/l	ppm
Halon 1301	5075	834,000	86	14,000
Halon 1211	2200	324,000	52	7,650
Halon 2402	1340	126,000	17	1,600
Halon 1202	470	54,000	16	1,850
Halon 1011	340	65,000	20	4,000
Halon 104	180	28,000	2	300

(4) Application of Data to Practical Situations

Toxicologists often define vapor concentrations in volume (molar) per cent or parts per million when expressing acute exposure data as in Figures 21 and 22. However, for practical purposes it is of interest to plot the same data of Figures 21 and 22 on a weight per unit volume basis. In this case, pounds of agent per 1000 cubic feet were used and this results in Figures 23 and 24. This now shows the relative hazard present if equal weights of agent were discharged into a confined area. A comparison of this type is extremely useful in gaining perspective of the huge amounts of some of the agents required before hazardous concentrations occur. In the case of Halon 1211 for example, 110 pounds would have to be vaporized in a 1000 cubic feet area before lethal conditions would be reached for fifteen minute exposure. Since Halon 1301 apparently kills by displacement of oxygen only, concentrations exceeding 50% must be reached in order to be quickly lethal. This represents about 180 pounds per 1000 cubic feet, and except for storage areas seems of very little practical concern.

FIGURE 23

Comparison of Acute Vapor Toxicity of Candidate Agents
Single Exposures Causing Essentially No Mortality
(LCT 0) to Rats

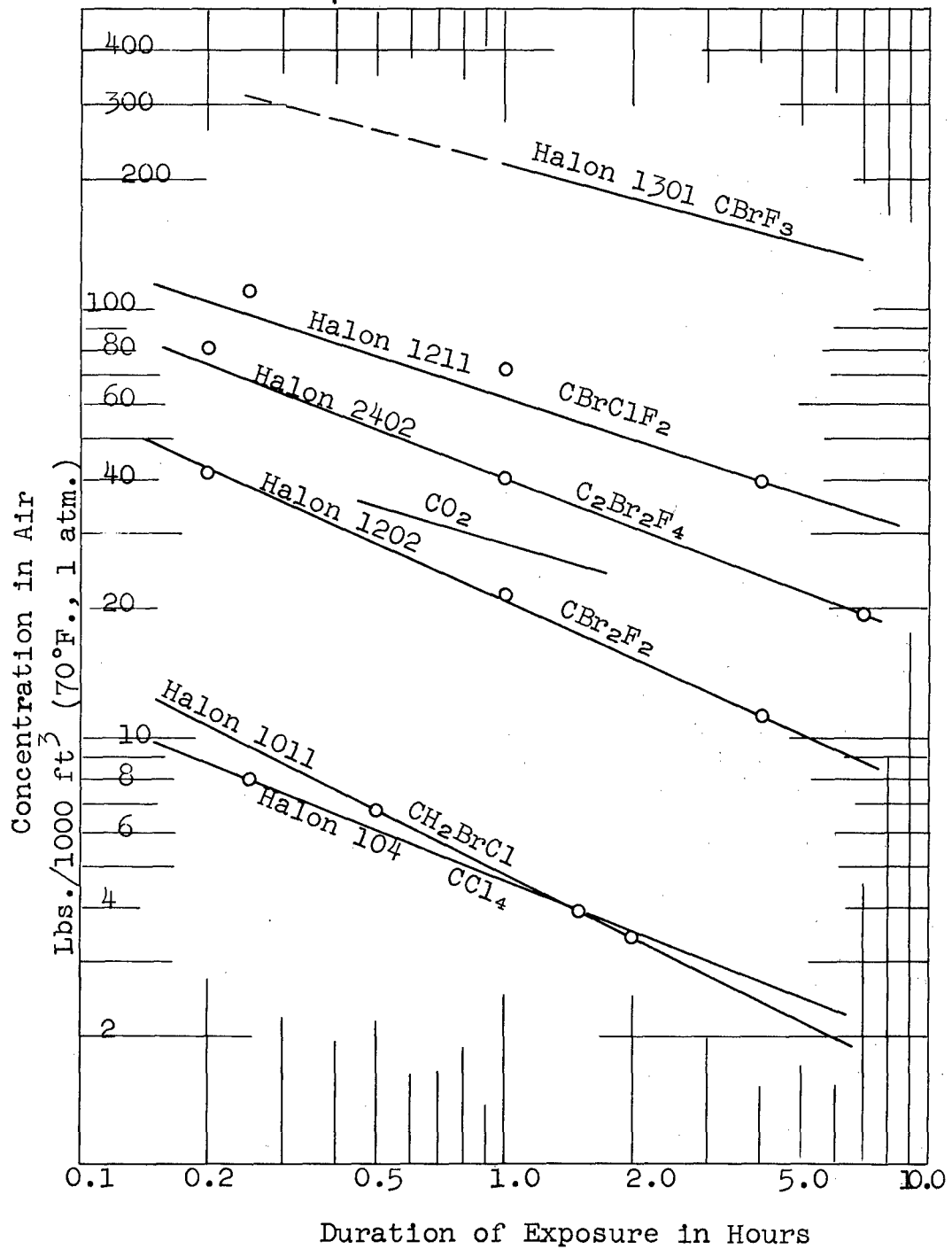


* Army Chemical Center ⁵⁶ (Approximate Lethal Concentration)

FIGURE 24

Comparison of Acute Vapor Toxicity of Candidate Agents

Single Exposures Causing Essentially No Mortality
(LCT 0) to Guinea Pigs



3. Results of Experiments and Pertinent Toxicological Data

A. Halon 1301 (bromotrifluoromethane) was not studied extensively in this project since the toxicity has been well defined in previously published data. Treon ⁵³ reported that seven hour exposures to a 33% concentration resulted in the death of only one rabbit in a group of thirty-one animals including four rabbits, ten rats, six guinea pigs, ten mice and one cat. The Army Chemical Center ⁵⁶ reports an ALC of 832,000 ppm, (83%) for a fifteen minute exposure to rats. It appears, therefore, that Halon 1301 has little physiological effect other than that resulting from displacement of oxygen and a practical limit of about 50% appears realistic for humans. Such a concentration would require the escape of 180 pounds of material in a 1000 cubic foot room. It does not seem possible that hazardous conditions could occur outdoors and only remotely possible that they could occur in an enclosed area.

Because of its low boiling point, evaporation of Halon 1301 could result in freezing of the skin and eyes if contact occurs.

B. Halon 1211 (bromochlorodifluoromethane) has a very low acute vapor toxicity. To exceed the minimum lethal concentration for a fifteen minute exposure, about 110 pounds would have to be vaporized in a 1000 cubic foot room. The cause of death appeared to be due to anesthesia although tremors and convulsions occurred in high concentrations. Animals removed from exposure before death generally recovered quickly. At a concentration of 9.4% by volume, rats quickly recovered from a 6 1/2 to 7 hour exposure with no gross pathological changes other than slight lung congestion noted. Guinea pigs were less consistent in response, and generally more affected by equal exposures. Lung congestion was the only pathology in the guinea pigs which could be attributed to the exposure.

This material should not present a problem from skin absorption because of its high volatility. It does cause a slight chilling sensation but little else if spilled on the skin. No eye irritation other than chilling was seen in a rabbit in which both eyes were exposed to several milliliters of liquid Halon 1211. ⁵⁴

C. Because of the difficulty in obtaining sufficient high quality samples of Halon 2402 (1,2-dibromo-1,1,2,2-tetrafluoroethane) fewer animals were exposed to this compound than to the other compounds. However, it was possible to determine the exposures causing essentially no mortality. It was found that about ~~thirty~~⁵² pounds would have to be vaporized in a 1000 cubic foot room in order to exceed the minimum concentration which might be lethal in fifteen minutes. Death in rats appeared to be due to anesthesia. Guinea pigs were significantly more resistant to central nervous system effects but both species, particularly the guinea pigs, showed evidence of adverse effects on the kidneys.

Skin irritation studies ⁵⁴ with this material indicate that it should present no problem from skin contact or absorption under reasonable conditions of use.

D. Halon 1202 (dibromodifluoromethane) has a low acute vapor toxicity with only a slight capacity to cause organic injury. However, severe tremors and convulsions were seen almost immediately in animals introduced into a concentration of 2% in air. This corresponds to about eleven pounds per 1000 cubic foot. Although it is often difficult to extrapolate animal data of this nature to humans, it must be assumed that this compound is probably a convulsant at exposure levels approaching 2% by volume. This data confirms previous work reported by the Army Chemical Center ⁵⁸.

The material should not present a problem from skin absorption because of its high volatility.

E. Halon 1011 (bromochloromethane) has a moderate acute vapor toxicity and only a very slight capacity for causing liver injury. Injury that does occur is characterized by fatty changes with none of the fibrotic changes seen in animals exposed to carbon tetrachloride ^{48,60}. It is an anesthetic of moderate intensity but of prolonged duration ⁴⁸. Deaths resulting from exposure to Halon 1011 took place during anesthesia or else recovery was complete. Guinea pigs were shown to be slightly more sensitive to this material than rats. About 8-9 pounds would have to be volatilized in a 1000 cubic foot room to exceed the concentration found to cause no mortality after a fifteen minute exposure.

It should be noted that the concentration causing no deaths in rats is well below that considered to cause mortality by the Army Chemical Center ⁵⁶ and may change the significance of some of the conclusions of that work.

Skin irritation studies indicate that this material is capable of causing moderate injury only if confined on the skin for long periods of time (several days) ⁵⁴. It should present no problem from skin absorption. Industrial experience indicates, however, that it causes a stinging, burning sensation if spilled on the skin. The mechanism of this phenomenon is not well understood but it is a property of many solvents, and although very unpleasant, is not particularly hazardous.

F. Halon 104 (carbon tetrachloride) is reported primarily as a standard for comparison. The toxicity resulting from acute exposures of rats to carbon tetrachloride was determined on animals from the same colony by Adams, et al ⁶³. Exposures causing no mortality are plotted on the summary graphs, Figures 21 and 23. Comparable data for guinea pigs was not available in the literature. Sufficient exposures were conducted during this study to establish the toxicity toward this species and are summarized in Appendix VI, page 114. Adams, et al ⁶³ reported that carbon tetrachloride was a potent hepatotoxin. Microscopic evidence of liver injury could be detected in animals exposed for seven hours to concentrations greater than 50 ppm. Injury resulted in fatty infiltration leading to fibrotic changes and cirrhosis.

Guinea pigs appear to be slightly more resistant to acute exposures to carbon tetrachloride than rats on the basis of kill and survival but considerable liver pathology was noted in animals examined grossly. About five pounds of Halon 104 per 1000 cubic feet is required to exceed the concentration causing no mortality from a fifteen minute exposure.

An LD 50 for rabbits for 24 hour skin absorption under a cuff has been determined as 1.8 g/kg with 19/20 confidence limits of 1.0 to 3.1. The material has effect on the skin typical of organic solvents and is only slightly irritating to the eyes ⁵⁴.

4. Summary

The summary graphs presenting the exposures causing essentially no mortality to rats and guinea pigs, show that the results are generally consistent with the

small amount of toxicological data that has been published previously. For convenience, the ALC's reported by the Army Chemical Corps ⁵⁶ have been included on the graphs for rats and the only serious discrepancy between the data is in the position of Halon 1011 (bromochloromethane). It appears that the ALC of 65,000 ppm is too high on the basis of the data accumulated in the present study. This is confirmed by the data of Comstock, Fogelman and Oberst ⁵¹ who found no deaths occurring from fifteen minute exposures to less than 27,000 ppm. The reason for this discrepancy is not obvious but possibly reflects the hazard of basing conclusions on too few animals in a very limited experiment. There is general agreement between the results of exposures of guinea pigs and rats. The ranking of the compounds is in complete agreement with the two species, and with the exception of carbon tetrachloride, the relative distances between lines representing similar criteria are approximately the same. This rather close agreement between species gives a higher degree of certainty to the extrapolation of this data to other species, including man, particularly as far as expected organic injury is concerned. Man, having a more highly developed nervous system, could conceivably show differences in response of the central nervous system at lower concentrations. More extensive toxicological studies on animals should be undertaken before one would attempt any experiments on human subjects.

Three observations must be considered in addition to the data presented on the charts:

1. Carbon tetrachloride (Halon 104) has a severe effect on the liver. Adams, et al, ⁶³ have shown that the maximum concentration for a seven-hour exposure without detectable organic injury is 50 ppm. It is this capacity to cause liver injury which has caused many of the deaths attributed to carbon tetrachloride. None of the other five compounds have such a capacity to cause organic injury.

2. Although relatively low in acute vapor toxicity (1,2-dibromo-1,1,2,2-tetrafluoroethane) (Halon 2402) produced obvious damage to the kidneys of the guinea pigs and rats, whereas the other compounds studied produced no significant organic injury.

3. Halon 1202 (dibromodifluoromethane) produced pronounced effects upon the central nervous system even at the lowest concentration tested, 2%. No attempts were made to determine the lower limit of this response because of the difficulty in extrapolating such data to human subjects.

Considerable emphasis has been placed on the Underwriter's classification of materials on the basis of vapor toxicity. It is summarized as follows:

TABLE 19

UNDERWRITER'S LABORATORIES' CLASSIFICATION OF
COMPARATIVE LIFE HAZARD OF GASES AND VAPORS

<u>Group</u>	<u>Definition</u>	<u>Examples</u>
1	Gases or vapors which in concentration of the order of 1/2 to 1 per cent for duration of exposure of the order of five minutes are lethal or produce serious injury.	Sulfur Dioxide
2	Gases or vapors which in concentrations of the order of 1/2 to 1 percent for durations of exposure of the order of 1/2 hr. are lethal or produce serious injury.	Ammonia Methyl Bromide (Halon 1001)
3	Gases or vapors which in concentrations of the order of 2 to 2 1/2 per cent for durations of exposure of the order of 1 hour are lethal or produce serious injury.	Carbon tetra- chloride chloroform
4	Gases or vapors which in concentrations of the order of 2 to 2 1/2 per cent for durations of exposure of the order of 2 hours are lethal or produce serious injury.	Methyl Chloride Ethyl Bromide
5	Gases or vapors much less toxic than Group 4 but more toxic than Group 6.	Methylene Chloride Carbon Dioxide Ethane, Pro- pane, Butane
6	Gases or vapors which in concentrations up to at least about 20 per cent by volume for durations of exposure of the order of 2 hours do not produce injury.	Freon 12 Freon 114

This system can be criticized because of its extremely broad groupings but it does allow one to separate into rather general classes.

Applying the Underwriters' system to the data which has been presented in this report the following classifications seem proper:

Halon 1301 (CBrF ₃)	Group 6
Halon 1211 (CBrClF ₂)	Group 5
Halon 2402 (C ₂ Br ₂ F ₄)	Group 5 or 4
Halon 1202 (CBr ₂ F ₂)	Group 4
Halon 1011 (CH ₂ BrCl)	Group 3
Halon 104 (CCl ₄)	Group 2

It should be noticed that on the basis of the data of Adams, et al ⁶³, carbon tetrachloride has been dropped from the assigned group of 3 to group 2, since that it was felt that the liver injury which occurred in rats should be interpreted as a severe effect.

Carbon dioxide, CO₂, has an Underwriters' classification of group 5. This classification is well justified, but CO₂ must not be considered to be without pronounced physiological effect. Anesthetic effects begin at concentrations of 10% according to published data and increase in severity through unconsciousness, finally resulting in deaths occurring after only a few minutes exposure ⁴⁹ to concentrations in the range of 20 to 30%. Using carbon tetrachloride as a standard it is apparent that all the agents studied are considerably lower in toxicity and undoubtedly present much less hazard. It seems possible then, to place the subject materials in an order of increasing toxicity based primarily on exposures causing essentially no mortality.

a. Halon 1301 has been shown to be practically innocuous from acute inhalation ⁵³, ⁵⁶. Concentrations must be capable of reducing the oxygen level below safe limits before injury is likely. It is the obvious choice in systems where it can be used successfully. It has an Underwriters' rating of 6. Because of its low boiling point freezing of the skin and eyes can occur if exposed to the liquid.

b. Halon 1211 appears to present little hazard in applications where its physical properties are desired. It would fall into the upper half of the Underwriters' rating of 5. The hazard from skin and eye contact is very low.

c. Halon 2402 appears to offer a slight hazard from inhalation although it is certainly low in acute vapor toxicity. The capacity to produce kidney injury should be investigated further before any exposures to humans are likely. It would probably fall into the lower part of Underwriters' group 5 and possibly the kidney pathology noted in animals autopsied would suggest a rating of 4. It has only a slight effect on the skin and eyes.

d. Halon 1202 has a low acute vapor toxicity but does produce severe effects on the central nervous system at levels easily attainable. The central nervous system effect appears severe enough to seriously impair the judgment and coordination of anyone excessively exposed. Based on the data presented herein, an Underwriters' classification of 4 is proper.

e. Halon 1011 has a moderate, relatively long lasting narcotic effect, but only a slight capacity to cause organic injury. It is roughly only $1/2$ to $1/3$ as toxic as carbon tetrachloride on the basis of exposures causing essentially no mortality. Underwriters' Laboratory has assigned a rating of 3 to this compound. Although unpleasant when spilled on the skin or eyes such contact is not hazardous to health.

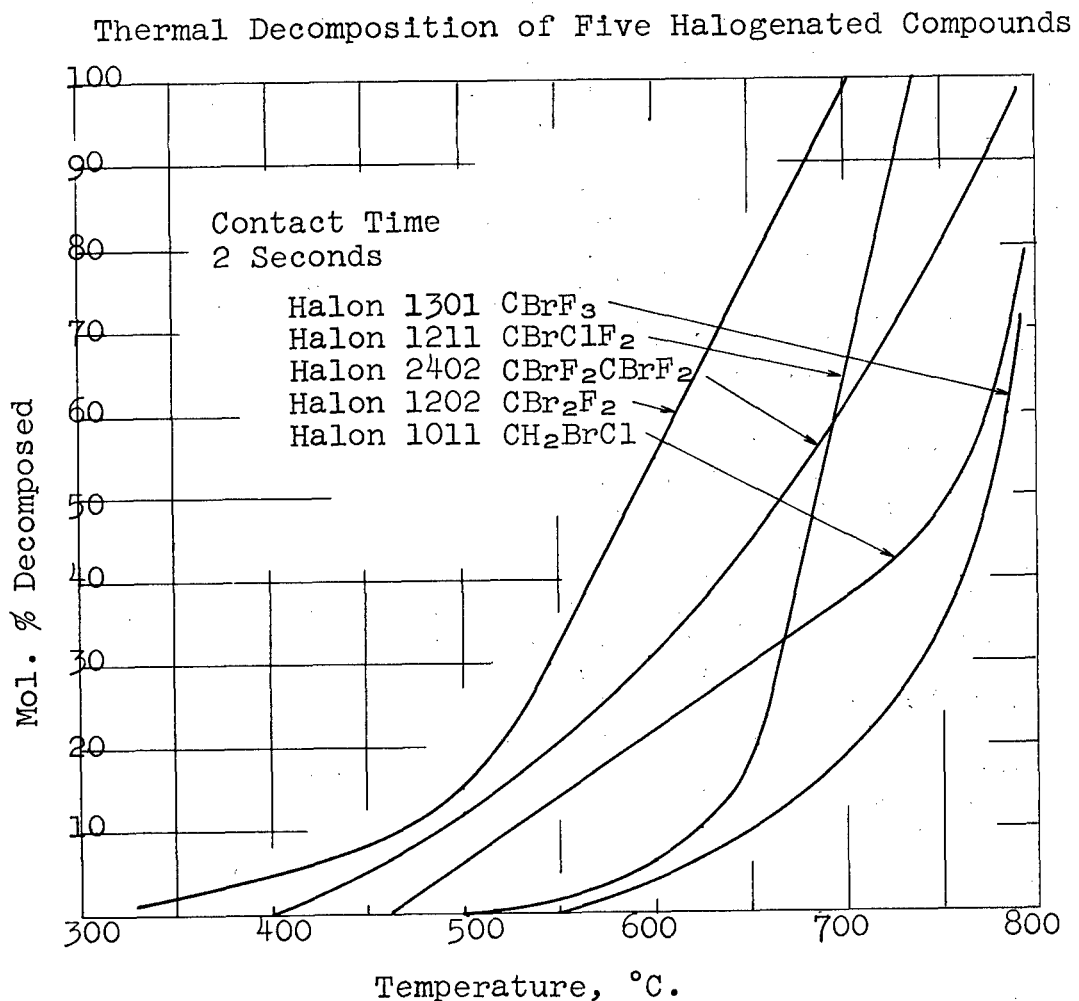
f. Halon 104 (carbon tetrachloride) was included in this series only as a reference compound. Death and injury attributed to its use in fighting fires have, in many cases, been exaggerated and are usually a result of gross mishandling. Nevertheless the material does have the capacity to cause serious effects. Underwriters' has classified this material as group 3 but a classification of group 2 seems more logical on the basis of organic injury to rats.

D. Thermal Stability of Agents

Analysis of the limited data ^{53, 56, 61} available on the thermal decomposition products of halogenated agents indicate that these products are similar for all of the agents. They include the halogen acids (hydrochloric, hydrobromic, and hydrofluoric); the free halogens (chlorine and bromine but not fluorine); carbon monoxide and various halogen analogs of phosgene (COCl_2). Examples of these analogs would be COFCl , COF_2 , COFBr , etc. All of the above compounds have very high toxicities, and it is fortunate that adequate warning properties go hand in hand with these products of decomposition.

One of the common methods of evaluating the toxicity of decomposition products is to pass the compound through a hot tube and either subject test animals to the effluent stream or else chemically analyze this stream to obtain an idea of its toxicity. Since similar compounds are found in the decomposition products of all halogenated agents, this method actually determines the thermal stability of the agents. Fortunately, the extent of thermal decomposition is directly proportional to the pyrolyzed toxicity for all the agents in question (methyl bromide is a notable exception). Therefore, this method gives a relative idea of the problems presented. The results should be interpreted with caution, however, since they are a function of the temperature used as can be seen from Figure 25.

FIGURE 25



In this work a mixture of 2.5 volume per cent agent and anhydrous air was passed through a 0.21 inch I.D. by 24 inch long 304 stainless tube. The tube was inserted inside a 15 inch long furnace and the temperature was measured with a chromel alumel thermocouple inserted in the annular area between the tube and the furnace. This is a common method of measuring gas temperatures in the laboratory but results in a measured temperature that is higher than the actual gas temperature. The gas air flow was maintained at 200 cc per minute which corresponds to a contact time of about 2.2 seconds. Since a contact time of one second was used by the Army Chemical Center ⁵⁶, it is unlikely that the actual gas temperatures reported by them approached as close to the recorded temperature as in this work.

After passing through the pyrolysis tube, the gas was passed through antimony trisulfide and silver nitrate which removed the free halogens and the halogen acids, respectively. A gas interferometer and a gas chromatographic unit completed the train and were used to measure the extent of decomposition.

Figure 25 shows that the initial decompositions occur at from 330°C. to 610°C., but that at about 800°C. all agents are completely pyrolyzed. It should be noted that the material of construction of the tube can be important since corrosion of the tube forms ferric halides which are active decomposition catalysts for many organic compounds.

The agents may be ranked as follows in order of decreasing thermal stability, Halon 1301, 1211, 1011, 2402 and 1202. The toxicities after pyrolysis ⁵⁶ in order of increasing toxicity are Halons 1301, 1211, 1011, 1202 and 2402. As far as the practical implications of these relative thermal stabilities are concerned, it is of interest to note that Ansul ²² reports Halon 1202 to have caused considerable trouble in their five tests because of this decomposition, but apparently the other agents studied did not show this. Some laboratory studies also show that Halon 1202 and Halon 2402 decomposed almost instantaneously in the apparatus used 18, 19.

E. Stability on Handling and Storage

Air Force requirement number 4 is that the agent should be stable on handling and storage for up to five years. Since the agents can be stored in either

the shipping container or the extinguishing system, long term contact with a large number of metals and elastomers is probable. Since five year corrosion and swelling tests are impractical, tests are usually conducted under conditions that accelerate corrosion and swelling. This is normally done by increasing the temperature to which the specimen and agent are subjected. Tests under both anhydrous and wet conditions are run, because the recharging of extinguishing equipment in the field can introduce water into the system.

The Purdue Research Foundation 5 investigated the corrosion of various metals by many of the compounds in their comprehensive screening program. All five agents of this study were not included, however. In the accelerated tests polished and weighed strips of the metal and 20 ml of the agent were sealed in glass ampoules (Carius tubes) and subjected to a temperature of 200°C. (392°F.) for thirty days. The physical condition of the test strips were noted and after surface coatings were removed, the strips were reweighed. The results may be summarized as shown in Table 20

TABLE 20
CORROSION TESTS
PURDUE RESEARCH FOUNDATION
392°F. for 30 days

System	Weight of Metals, g		Change in Wt.		Appearance
	<u>Initial</u>	<u>Final</u>	<u>g</u>	<u>%</u>	
Halon 1011					
Copper	1.8078	0	-1.8078	-100	Completely corroded
Aluminum	1.1758	0.6501	-0.5257	-45	Corroded
Iron	2.7196	2.7351	+0.0156	+1	Red coating
Halon 1301					
Copper	1.8290	1.8398	+0.0108	+1	Slight discoloration
Aluminum	1.2101	1.2110	+0.0009	nil	No discoloration
Iron	3.1116	3.1170	+0.0054	nil	Slight discoloration
Halon 2402					
Copper	1.7443	1.5442	-0.2001	-11	Gray coating
Aluminum	1.4465	0	-1.4465	100	Completely corroded
Iron	2.9080	2.9043	-0.0037	nil	Black coating

The excellent stability of Halon 1301 was shown by these tests. Further tests 5, at lower temperature, were performed on those compounds that showed instability at 392°F. Of the five candidate agents, only Halon 2402 was included in these later tests, which were run at 200°F. (93°C.) for thirty days. The results for Halon 2402 were as follows:

TABLE 21
CORROSION TESTS
PURDUE RESEARCH FOUNDATION

200°F. for 30 Days

System	Weight of Metals, g		Change in Wt.		Appearance
	<u>Initial</u>	<u>Final</u>	<u>g</u>	<u>%</u>	
Halon 2402					
Copper	1.8852	1.8852	0	0	No discoloration
Aluminum	1.1781	1.1781	0	0	"
Iron	3.4582	3.4582	0	0	"
Brass	3.8064	3.8053	-0.0011	nil	

Halon 2402 was thus shown to be very stable at 200°F. but unstable at 392°F. for a 30 day period in the presence of copper and aluminum.

A much more extensive stability program is reported by the duPont Company 6. In this work, steel, brass and aluminum test samples were heated in the presence of the agents. The agents were anhydrous in one series of tests, and three volume per cent of water was added in the second series. This amount of water is beyond the solubility in all cases so a separate aqueous phase existed in the wet tests. The time of exposure was 260 days and the temperature was 120°C. (248°F.). Penetrations were reported in inches per month. The negative values reported for Halon 1301 indicate a tightly bound scale on the surface of the metal specimen. The results are summarized in Table 22.

TABLE 22

PENETRATION OF METALS
E. I. DUPONT DE NEMOURS

260 Days at 248°F.

Average Penetration in inches/month $\times 10^{-6}$

Agent	Aluminum		Brass		Steel	
	Anhy- drous	3% H ₂ O	Anhy- drous	3% H ₂ O	Anhy- drous	3% H ₂ O
1301	0.7	59	1.5	-35	0.9	-91
1211	0.8	54	6	435	1.1	82
1202	0.7	55	0.7	375	0.8	62
2402	0.4	50	5.7	385	1.5	140
1011	>1500	>1500	200	1620	27	280

The acceleration of corrosion in the presence of water is apparent from the above data. The marked superiority of the fluorinated agents over Halon 1011 in the above systems is also evident.

Some other corrosion studies with Halons 1301, 1202 and 1011 in the presence of other metals have been conducted ⁵⁴. In these tests, metal strips with a surface area of 2 1/2 square inches were sealed in glass ampoules at 30°C. for 30 days. Both dry and wet agents were used. Where water was used, one weight per cent was added which was enough to exceed the solubility, and a separate aqueous phase resulted. In this case the penetrations are reported in mils/year. A minus sign does not indicate penetration but instead that the metals increased in weight due to scale formation.

TABLE 43
CORROSION OF METALS
30°C. for 30 Days

Metal	Penetration, mils per year					
	Halon 1301		Halon 1202		Halon 1011	
	<u>Wet</u>	<u>Dry</u>	<u>Wet</u>	<u>Dry</u>	<u>Wet</u>	<u>Dry</u>
25 Alum- inum 85/15	0.032	0.032	1.3	0.053	Dis	0.064
Brass	-0.013	0.044	-0.020	0.0068	0.358	0.149
Copper	0.130	0.065	-0.0065	0.000	0.166	0.078
Iron	-0.62	-0.064	2.50	0.012	0.342	-0.018
Mag- nesium, FS	2.83	-0.0023	-1.40	0.016	1.098	0.499
Monel	0.045	0.024	0.029	0.029	0.068	0.088
Nickel 304	0.00	-0.003	0.006	0.013	0.029	0.042
Stain- less	0.014	-0.011	0.018	0.018	0.016	0.016
Tin	0.05	-0.035	2.44	0.005	0.770	0.015
Zinc	0.239	-0.012	Dis	0.239	0.596	0.290

Dis = metal completely disintegrated.

Examination of the specimens used in the wet tests showed most of the attack occurred at the agent-water interface. The practical significance of this is that local corrosion will probably occur in the container at the surface of the agent in the event of an inadvertent admission of water into the system.

In general, most metals can be used with any of these agents if the system is dry, although some metals cannot be recommended because the possibility of water is always present. The stability of Halon 1301 in a wet aluminum system is noteworthy. Those metals that are generally considered to be corrosion resistant, e.g., monel, nickel, and stainless, do not seem to be adversely affected by the presence of water.

Another property of interest is the attack or swelling of elastomers by the various agents. This becomes important in systems that have gaskets and hoses in contact with the agents for extended periods of time. The duPont Company 7 reports some elastomer swelling data on the agents of this study. Room temperature conditions were used, and the tests were run sufficiently long so that the maximum effect was observed. Their results may be tabulated as follows:

TABLE 24
SWELLING OF ELASTOMERS
Maximum Swelling in %
THE DUPONT COMPANY

Halon Numbers	1211	1202	1301	2402	1011
Elastomer					
Hycar OR-15	4.8	11.1	0.6	6.8	49.3
Perbunan 26	10.1	22.9	0	10.0	50.4
Neoprene GN-A	13.0	26.7	0.2	6.0	34.1
Hypalon E-7	7.2	29.0	2.3	9.8	40.0
GR-S	14.6	24.0	1.0	15.2	26.3
Natural Rubber	23.4	34.1	1.3	26.0	31.5
Butyl	2.3	47.0	2.0	24.0	14.7
Thiokol FA	4.1	7.9	0.3	4.0	--
Silicone 23	14.9	36.3	21.5	33.3	14.4

Halon 1011 completely disintegrated the thiokol FA test sample. Some other elastomer swelling work ⁵⁴ using Halons 1301 and 1202 was done under room temperature conditions for a 30 day period. Visual observation of the elastomer specimens was then made and the swelling reported as none apparent, very slight, slight, large or extreme. The results may be summarized as follows:

TABLE 25
ELASTOMER SWELLING
30°C. for 30 Days

<u>Elastomer</u>	<u>Halon 1301</u>	<u>Halon 1202</u>
Natural Rubber	Slight	Extreme
Silastic 50-24-480	"	Slight
" 80-24-480	"	"
" 181-4-480	none apparent	"
Neoprene GN	" "	"
Polyethylene	" "	none apparent
Silastic 152	Large	Large
Tygon	none apparent	very slight
Resisto Flex PVA	" "	none apparent
Butyl	very slight	Extreme
Teflon	none apparent	none apparent
Silastic 160	Slight	Large
Silastic 250	none apparent	Slight
Nylon	" "	none apparent
Saran	" "	" "
Kel-F	" "	" "

It is apparent from tables 24 and 25 that Halon 1301 presents little problem in the selection of elastomers. All the others require careful selection of the proper elastomers to use.

If the agents were to be ranked in a general fashion as far as the stability on storage in the presence of metals, moisture, and elastomers the ranking would be as follows:

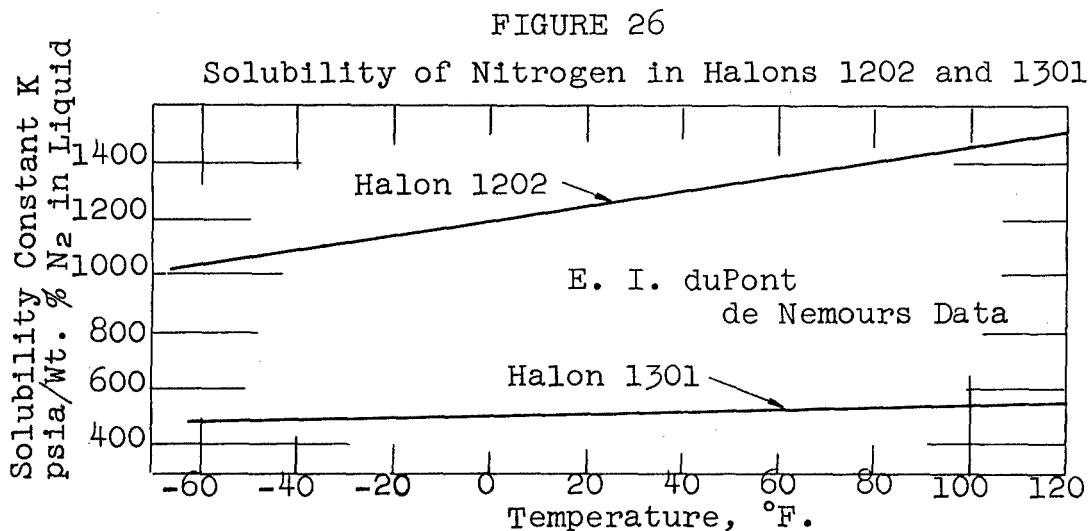
1. Halon 1301 (best at top)
2. Halon 1211
3. Halon 2402
4. Halon 1202
5. Halon 1011

F. Capability of Use as a Liquid

Air Force requirement five specifies that the agent must be a liquid or capable of being used as a liquid. Since all five agents have critical temperatures above the upper temperature requirement (130°F.), all are capable of being used as liquids. However, with the exception of Halon 1011, all of the agents exert greater than atmospheric pressure at 130°C. The equilibrium vapor pressure-temperature curves are given for the agents in Figure 1.

The normal method of furnishing the energy necessary to discharge a vaporizing liquid agent is through the use of a pressurizing gas such as nitrogen, dry air, or carbon dioxide. Nitrogen or air are frequently used because carbon dioxide does not furnish enough pressure at -65°F. to discharge the agent in an effective manner.

The solubilities of nitrogen in Halons 1301 and 1202 have been determined by the duPont Company 7. Since the solubility is a function of the temperature and pressure, the data were presented in graphical form which is reproduced here in Figure 26.



While the solubility of nitrogen on a weight basis is very small, the volumes of nitrogen that are dissolved per unit volume of liquid agent are, of course, quite large. For example, if Halon 1202 were pressurized to 400 psig with nitrogen at 70°F. and then discharged to the atmosphere, about five volumes of nitrogen would come out of solution per volume of liquid Halon 1202. In the discharge of Halon 1301 (and 1211 to a lesser degree) this effect is of less relative importance since the agents themselves are normally undergoing flash vaporizations upon discharge, with the resulting generation of a large amount of vapor.

The question of determining the extinguishing system pressure at +130°F. when sufficient discharge pressure exists at -65°F. is of interest. Since none of the five agents have sufficient vapor pressure at -65°F. to discharge properly, super pressurization is usually applied. Knowing the vapor pressure-temperature relationships and the total pressure (agent vapor pressure plus the nitrogen pressure) at one temperature, the pressure of the system at another temperature can be estimated fairly accurately by adjusting the vapor pressure of the agent for the new temperature and also the partial pressure of the nitrogen (corrected for the new temperature by the ideal gas law). Actually this method is only approximate since the pressures at different temperatures are a function of the fill ratio. A more refined calculation must include the amount of agent in the vapor phase, the amount of liquid in the liquid phase, the amount of nitrogen dissolved in the liquid phase and the amount present in the vapor phase. These refinements are of course dependent on the amount of agent and the size of the system, i.e., the fill ratio.

ERDL ¹² has experimentally determined system pressures at various temperatures for Halon 1301 at different fill ratios. The data are presented in graphical form from which the following points were taken:

TABLE 26

SYSTEM PRESSURES, PSIG
U. S. ARMY ERDL

Halon 1301, pressurized with nitrogen
to approximately 400 psig at 70°F.

Temperature, °F.	<u>Fill Ratio</u>	
	69#/ft ³	40#/ft ³
-65	125	115
0	220	210
70	390	380
130	775	530

It is apparent that the pressures are not too dependent upon the fill ratio until higher temperatures are reached.

Some other pressure temperature data are reported by the duPont Company ^{8, 9} for Halons 1301, 1202, and 2402. Both nitrogen and Halon 14 (Freon 14, or carbon tetrafluoride) were used as the pressurizing gases. They concluded that nitrogen was the more practical gas to use. The biggest disadvantage of nitrogen is that the pressure falls rapidly during discharge, although this can be overcome somewhat by using a lower fill ratio. Their results may be summarized as follows:

TABLE 27

PRESSURE TEMPERATURE RELATIONSHIPS
E. I. DUPONT DE NEMOURS

Agent	Pressurizing Gas	System pressure, psig		
		-65°F.	+77°F.	+130°F.
Halon	Halon 14	200	430	490
"	nitrogen	200	285	345
"	"	300	415	490
"	Halon 14	200	845	1200
"	nitrogen	200	425	685
"	Halon 14	200	460	565
"	nitrogen	200	265	305
"	nitrogen	400	520	585

Approximate figures that are obtained by the simplified method described above that neglects the fill ratio are as follows:

TABLE 28
CALCULATED SYSTEM PRESSURES, PSIG
PRESSURIZED WITH NITROGEN

Temp.	Halon 1301	Halon 1211	Halon 1202	Halon 2402	Halon 1011
-65°F.	140	269	285	290	292
0	268	324	335	341	343
70	400	400	400	400	400
130	651	496	470	459	454
-65	2.5	120	136	141	143
0	56	150	163	168	169
70	215	200	200	200	200
130	445	273	248	237	231

Notice that Halon 1301 cannot be used in a low pressure system that is operable over the Air Force temperature range of -65 to +130°F. This is the major reason fixed in-flight systems in the Air Force utilize Halon 1011 or Halon 1202 more than Halon 1301.

G. Freezing Point

Air Force requirement six is that the agent must have a freezing point below -65°F. All agents that comprise this study meet this requirement. The freezing points of the individual agents are given in Table 1.

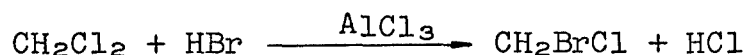
H. Relative Cost

Air Force requirement seven is that the agents must be capable of being produced in quantity within reasonable cost limits. The question of cost of a vaporizing agent is difficult to answer because it is a function of several variables. All manufacturing costs depend upon the amount produced to a large extent. Carbon tetrachloride is a cheap vaporizing liquid agent, not because such large amounts are consumed in this application, but because such large amounts are consumed as a chemical intermediate and as a solvent. As a result, the user of this material for fire extinguishing purposes gets the benefit of large volume production.

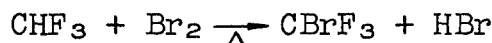
None of the five agents that comprise this study have any other commercial uses of importance at present and do not seem to have much potential along these lines. Halon 1301 has properties that make it of interest as a low temperature, one stage, refrigerant but this would be a very limited market.

The normal methods of manufacture of these agents, starting from readily available commercial compounds, are:

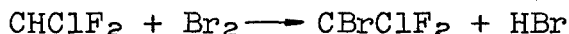
Halon 1011



Halon 1301

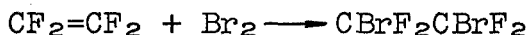
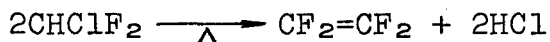


Halon 1211



The similarity of processes for Halons 1301 and 1211 is apparent. The first reaction shown for Halon 1211 is the present commercial process for making CHClF_2 , a refrigerant and propellant with the trade marked names of Freon 22, Genetron 22, Ucon 22 or Iseon 22.

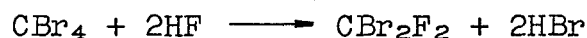
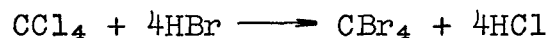
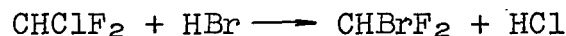
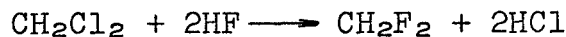
Halon 2402



Here again the first step is a present commercial process and so is the second step which yields the monomer for Teflon, a duPont fluorocarbon plastic.

Halon 1202

Several methods are available for manufacture of this agent. The relative merits of these methods depend upon the production volume and other factors.



If the agents were to be ranked in order of increasing cost at relatively large and comparable consumption rates, they would rank as follows:

Halon 1011

Halon 1211

Halons 1301, 1202, 2402

The positions of Halons 1202 and 2402 are less well defined since they are made by dissimilar routes but they would probably be comparable in cost to Halon 1301. Of course, this ranking does not hold for pilot plant quantities or small quantities which may be governed by a by-product situation.

SECTION V

APPLICATION TECHNIQUES

In general, vaporizing liquid agents can be applied in three discharge patterns, straight stream, conical spray, and fan or flat spray. In the case of a low boiling point agent all three patterns may not be possible. For example, Halon 1301 cannot be discharged in a straight stream or a flat spray (unless refrigerated) because so much of this agent vaporizes upon discharge. As a result a conical pattern is the only practical one for this agent. The particular equipment used for Halon 1301 on the 50 square foot spill fire was the Army-developed nozzle for the 50-pound wheeled unit. This gave a conical pattern of very small droplets suspended in a large amount of vapor. The general appearance of this pattern was similar to that of carbon dioxide. This nozzle had a discharge range of about ten feet when using a 400 psig system pressure and had a discharge rate of slightly over one pound per second. This seemed to be a fairly optimum system for this flow rate and agent.

The boiling points of Halons 1011 and 2402 are high enough so that all three general patterns are available. In most fire situations the straight stream is not effective, so in a practical sense only two patterns are of interest for these agents. The best pattern depends upon the fire geometry. The fan pattern is undoubtedly the best for the spill fire since this is primarily a horizontal fire. The fan can be wide enough to cover the width of the spill, and then results are not very dependent upon operator technique since no lateral movement of the nozzle is necessary. Such a horizontal fan is obviously not a good pattern for the spilling fuel fire which is primarily vertical in configuration. In this case a wide conical pattern is about the best application form.

Halon 1211 is not capable of being discharged in a straight stream unless refrigerated because of its boiling point (+25°F.). This agent gives a discharge stream at normal temperatures that includes a higher percentage of liquid droplets than Halon 1301. These droplets are not as evident if high nitrogen pressurization (400 psig) is used with this agent. Under these conditions the agent application pattern is very similar to that of Halon 1301 except then it is not as effective an agent. Better results with this agent were obtained at lower pressurizations (200 psig) which gave discharge patterns with fairly large droplets. These

droplets could be seen falling out of the discharge stream into the fuel. This is believed to be the reason that reflash was not a serious problem with this agent on the 50 square foot spill fire and the spilling fuel fire.

Halon 1202 with a boiling point of 68°F. acts similar to Halon 1211 if the ambient temperature is high and similar to Halons 1011 and 2402 if the ambient temperature is low. Even at high ambient temperatures, however, a major portion of this material remains as a liquid upon discharge.

One of the problems inherent in vaporizing liquid agents is that of discharge range. Good ranges can be obtained with the higher boiling point agents such as Halon 1011 and 2402, when discharged in a straight stream. Unfortunately, a straight stream pattern is also the least effective in extinguishing the fires. Of the five agents in this study, Halon 1301 gives the most difficulty in obtaining good range although at higher discharge rates the ranges are fair. For example, a 20 gpm (4.37 lb./sec.) handline nozzle has a maximum range of about thirty feet with Halon 1301. No application rates of that magnitude were used in this study, but it was found that at equivalent rates the obtainable range was a direct function of the boiling point of the agent. This was to be expected, of course. If a fairly long range is desired along with a high degree of agent effectiveness, a long conical pattern is the best compromise. In fire extinguishing systems where several patterns are possible the operator will have a more effective fire fighting tool if he can use the best pattern for the hostile fire situation.

For Halon 1011 both flat sprays and conical patterns are effective. The choice between them depends upon the geometry of the fire. For Halons 1301 and 1211 conical patterns are the best compromise. An elliptical cross section pattern such as that available with some dry chemical nozzles would give good results in that the major axis of the ellipse could be turned as desired. In other words, a pattern with more of a horizontal than a vertical dimension could be used on the spill fire and the nozzle could also be turned 90°C. so that a pattern with more of a vertical than a horizontal dimension could be used on a fire that is essentially vertical, e.g., the spilling fuel fire.

The development of a discharge nozzle that gives an elliptical-conical pattern was not within the scope of this project. Such a discharge pattern would be about the best compromise available when questions of range and fire configuration are considered.

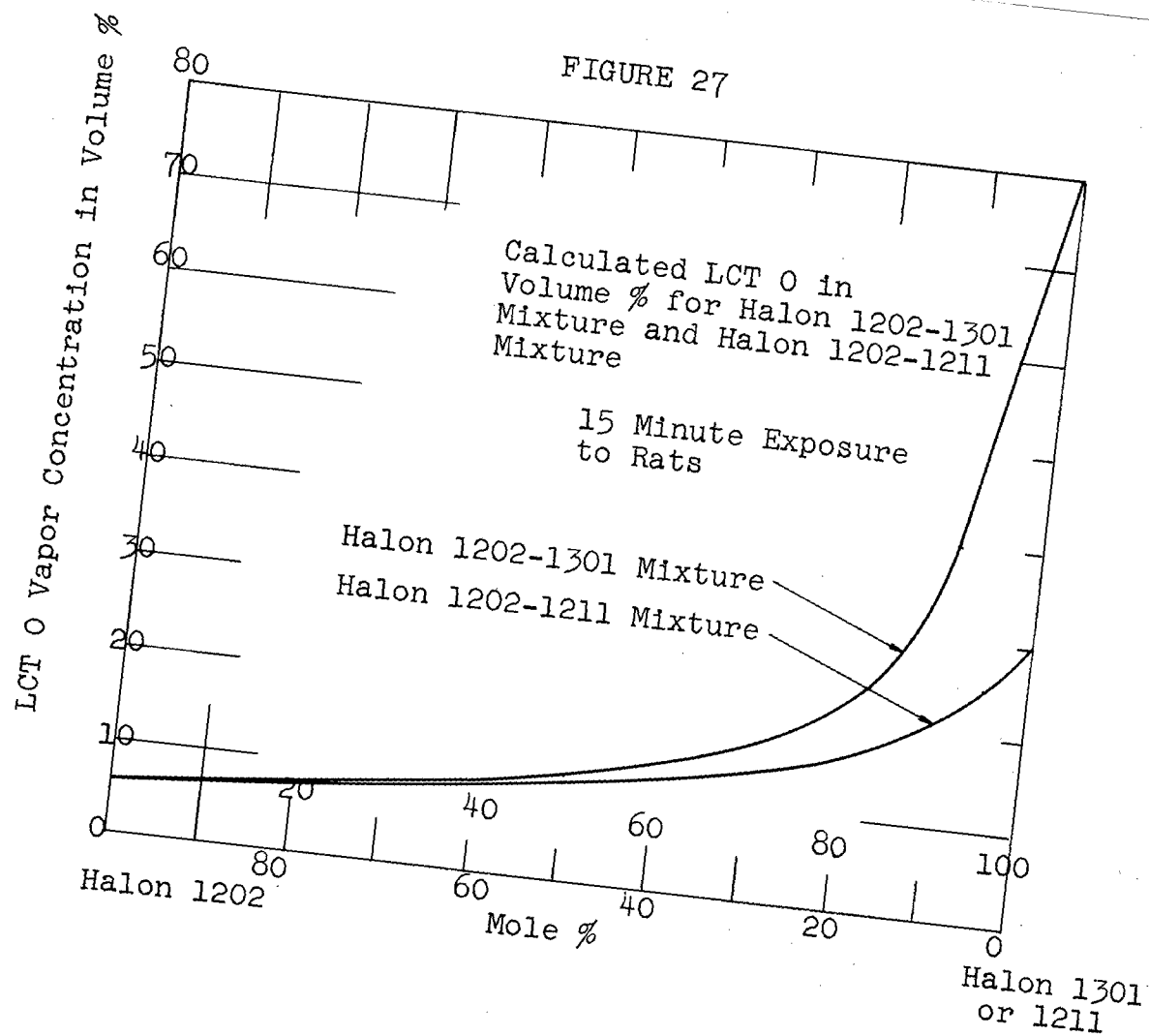
SECTION VI AGENT MIXTURES

At the beginning of this study it was believed that mixtures of agents might be the answer to the reflash problem that was experienced with Halon 1301 by the Rockwood Sprinkler Company in their work on the MB-3 truck. Such mixtures were to contain high and low boiling point agents. It was known from previous work⁵ that no marked improvement in flame inhibition properties was found with various mixtures. So no increase in effectiveness was expected but it was thought that the presence of a higher boiling point agent might prevent reflash.

Mixtures of agents have certain inherent disadvantages, however, one being that it is never certain just what mixture is present. If two agents of widely different vapor pressures are exposed to a leaking system in shipment, storage or in the final extinguisher, the composition of the mixture changes. Under extreme conditions the low boiling component will be lost to such a large degree that the properties of the remaining liquid (particularly the toxicity and the discharge characteristics) will be drastically changed.

The computed toxicities of Halons 1211 and 1202 mixtures are shown in Figure 27 as well as mixtures of Halons 1301 and 1202. Such calculated toxicities assume the lack of synergistic effects, which is probably fair since the physiological mechanisms by which these agents act are similar. The fact that the toxicity composition relationship is not linear is evident if one thinks about it, i.e., a 50/50 mixture cannot be better than twice as good as the most toxic component. And a 75/25 mixture would be 1/4 as toxic as the most toxic component (25%) only if the other component (75%) were completely innocuous. This is a somewhat unfortunate situation for the Halon 1211/1202 mixture since such a mixture (about 90 mol % 1211 and 10 mol % 1202) does arise naturally in the usual process of manufacture.

When it was found that the reflash problem was minimized with Halon 1211 as compared to Halon 1301 no further work was done with mixtures. Proper design of application systems with Halon 1211 is a better way of solving the reflash problem than is the use of mixtures which destroy the excellent toxicity picture of Halon 1211.



APPENDIX I

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APPENDIX II

NOMENCLATURE OF SELECTED AGENTS

Chemical Name	Bromo- chloromethane	Dibromo- difluoromethane	Bromo- trifluoromethane	Bromochloro- difluoromethane	1,2-dibromo- tetrafluoroethane
Chemical Formula	CH ₂ BrCl	CBr ₂ F ₂	CBrF ₃	CBrClF ₂	CBrF ₂ CBBrF ₂
Halon No.	1011	1202	1301	1211	2402
Freon (R)	30B1	12B2	13B1	12B1	114B2
	CB, CBM Methylene Chlorobromide	DB DBDF			

Halon System: The first digit refers to the number of carbon atoms in the molecule, the second digit is the number of fluorine atoms, the third digit is the number of chlorine atoms and the fourth digit is the number of bromine atoms. Hydrogen atoms are not counted, and if iodine is present, it is represented by a fifth number which is eliminated in the absence of iodine. Saturated compounds are understood. **Terminal zeros are eliminated.**

This system was first proposed by ERDL and a more detailed description of the system appears in reference 4.

The Freon name is a registered trade mark of the duPont Chemical Company. The system, briefly, is this: The first digit is one less than the number of carbon atoms in the molecule. In the case of methanes, the first digit is zero and eliminated. The second digit is one more than the number of hydrogen atoms in the molecule. The third digit is the number of fluorine atoms and unfilled valences are understood to be chlorine. The system was not originally meant for bromine containing compounds and in this case a supplemental B is used followed by the number of bromine atoms in the molecule.

APPENDIX III

FLASH VAPORIZATION CALCULATION

Halon 1301 from

Initial conditions: Liquid under pressure, 70°F.
to Final conditions: Liquid and vapor, atmospheric pressure, -72°F.

The calculations are simplified by assuming the process is essentially adiabatic; i.e., no heat is absorbed from container, valve, etc. Also, consider specific heat of liquid to be not a function of pressure.

The process can be considered in two steps:

1. Cooling of liquid Halon 1301 from 70 to -72°F.
2. Evaporation of a portion of this liquid to the vapor state at -72°F.

Heat given up in Step 1 = Heat absorbed in Step 2 or

$$Q_1 = m \text{ cp } \Delta T = Q_2 = m(x) (\text{latent heat of vaporization})$$

$$m = (.206)(142) = m(x)(50.8)$$

$$x = \frac{.206(142)}{50.8} = .575 \text{ vapor, } \therefore .425 \text{ liquid.}$$

This is the minimum amount of vapor since any heat transferred to the agent by the dispensing equipment or the fire results in more vaporization.

In the case of Halon 1211

Initial conditions: Liquid under pressure, 70°F.
Final conditions: Liquid and vapor, atmospheric pressure, 25°F.

Using the same assumption but noting that the cooling process only goes to 25°F. in this case. Also, cp of Halon 1211 is estimated at 0.17 Btu./lb./°F. in this region. $M(\text{cp}) \Delta T = m(x) \text{ latent heat of vaporization. } m(0.17)(45^\circ) = m(x)(57.6).$

$$x = \frac{0.17(45)}{57.6} = 0.133 \text{ vapor, } 0.867 \text{ liquid.}$$

Again, this is the minimum amount of vapor possible under these conditions.

APPENDIX IV

FIRE TEST FUEL

The fuel used in all fire tests was a stove and lamp naphtha with the following properties:

1. Distillation Range -----	Initial	116°F.
	10%	153
	20%	170
	30%	187
	40%	202
	50%	215
	60%	227
	70%	239
	80%	254
	90%	278
	End Point	338
2. API Gravity -----	64.4	
3. Color -----	30 Saybolt	
4. Odor -----	Good	
5. Doctor Test -----	Sweet	
6. ASTM D 130 Copper Strip Test -----	Passes 3 hrs. at 122°F.	
7. Reid Vapor Pressure -----	6.3	
8. ASTM D 381 Gum Test -----	0.3	

APPENDIX V

SUMMARY OF SQUARE PAN TESTS

HALON 1011

Test No.	Fire Size Sq. Ft.	Rate Lb./Sec.	Agent Used, Lb.	Extinguishing Time, Seconds.	Application Time, Seconds	N ₂ psig.	Wind mph.	Temp. °F.	Orifice Size	Remarks
10078										
-1	5	0.473	1.65	2.8	3.5	150	10	70	3/32"	
-3	10	0.485	5.85	12.1	12.1-	150	10	70	3/32"	
-4	10	0.462	3.47	7.2	7.5	150	10	70	3/32"	
-9	5	0.273	1.91	6.8	7.0	150	10	70	5/64"	
11048										
-1	5	0.283	3.14	11.0	11.1	250	5	50	1/16"	Limit fire
-2	5	0.335	1.81	5.1	5.4	250	5	50	5/64"	
-6	7	0.315	4.72	14.6	15.0	250	5	50	5/64"	
-7	7	0.495	4.95	9.4	10.0	250	5	50	3/32"	
-8	7	0.614	3.44	5.1	5.6	250	5	50	7/64"	
-9	10	0.577	4.26	6.7	7.4	250	5	60	7/64"	
-11	10	0.754	5.59	6.8	7.4	250	5	60	1/8"	
-12	10	0.48	6.25	12.5	13.0	250	5	60	3/32"	
-13	10	0.30	4.61	15.0	15.4	250	5	60	5/64"	
-14	3	0.143	1.56	10.3	10.9	250	5	60	3/64"	Limit fire
-16	3	0.235	1.26	4.9	5.4	250	5	60	1/16"	
-15	3	0.081	4.51	N.O.	56.0	250	5	60	1/32"	
10248										
-4	5	0.22	4.81	N.O.	21.9	250	5	60	1/16"	

SUMMARY OF SQUARE PAN TESTS

HALON 1202

Test No.	Fire Size Sq. Ft.	Rate Lb./Sec.	Agent Used, Lb.	Extinguishing Time, Seconds		Application Time Seconds	N ₂ psig.	Wind mph.	Temp. °F.	Orifice Size	Remarks
				Seconds	Seconds						
10098											
-1	5	0.865	1.82	1.7		2.1	150	5	65	5/64"	Straight stream pattern Ditto
-2	5	0.53	4.06	7.5		7.7	150	5	65	3/64"	
-3	5	0.68	4.09	5.2		6.0	150	5	65	3/64"	Reflash, limit fire
-4	6	0.65	2.26	2.7		3.5	150	5	65	3/64"	
-5	7	0.53	3.42	5.5		6.4	150	5	65	3/64"	Limit fire
-6	7	0.64	3.7	5.2		5.8	150	5	65	3/64"	
-7	7	0.55	1.64	2.7		3.0	150	5	65	3/64"	Reflash
-8	7	0.64	2.44	3.1		3.8	150	1	65	3/64"	
-9	10	0.59	4.5	7.2		7.6	150	1	65	3/64"	Limit fire
-10	10	0.64	8.2	12.4		12.8	150	5	65	3/64"	
10148											
-1	10	0.594	7.06	11.5		11.8	150	4	65	5/64"	Limit fire
-2	10	0.875	3.5	3.5		4.0	150	4	65	7/64"	
-3	5	0.423	2.75	6.2		6.5	100	4	65	3/64"	Reflash
-4	5	0.322	3.5	10.2		10.85	50	4	65	3/64"	
-5	4	0.356	1.67	3.9		4.7	50	2	65	3/64"	Limit fire
-6	4	0.36	1.19	3.0		3.3	150	8	65	1/32"	
-7	4	0.445	.735	1.65		1.65	150	8	65	3/64"	Limit fire
-8	7	0.518	3.03	5.2		5.85	150	8	65	3/64"	
-9	4	0.097	1.84	18.2		19.0	150	8	65	1/64"	Limit fire
-10	2.5	0.074	.14	1.1		1.9	150	8	65	1/64"	
-11	3	0.136	.55	3.7		4.0	150	8	65	1/64"	Limit fire
-12	4	0.120	1.80	14.4		14.9	150	8	65	1/64"	

SUMMARY OF SQUARE PAN TESTS

HALON 1211

Test No.	Fire Size Sq. Ft.	Rate Lb./Sec.	Agent Used, Lb.	Extinguishing Time, Seconds	Application Time, Seconds	N ₂ psig.	Wind mph.	Temp. °F.	Orifice Size	Remarks
09118										
-2	3	.372	1.37	3.0	3.7	150	3	70	3/32"	
-3	4	.41	1.37	3.2	3.4	150	3	70	3/32"	
-5	5	.37	1.69	4.0	4.6	150	3	70	3/32"	
-6	6	.37	5.2	N.O.	14.0	150	3	70	3/32"	
-7	4	.26	3.26	12.5	12.6	75	3	70	3/32"	
-8	4	.27	1.67	5.8	6.2	75	3	70	3/32"	
09238										
-1	7	.373	5.16	13.4	13.4	150	8	70	3/32"	Limit fire
-2	7	.365	6.84	17.3	18.7	150	8	70	3/32"	Ditto
-3	6	.36	6.25	16.3	17.4	150	8	70	3/32"	"
-4	6	.55	2.66	4.3	4.8	150	8	70	1/8"	
-5	7	.41	2.41	5.3	5.8	150	8	70	1/8"	
-6	10	.56	11.59	20.0	20.6	150	8	70	1/8"	Limit fire
09268										
-1	7	.665	2.53	3.3	3.8	150	4	70	9/64"	
-3	10	1.1	5.16	3.2	4.7	150	4	70	5/16"	
10248										
-8	5	.204	.8	3.9	3.9	150	5	70		A-20 1 qt. extinguisher, mod.
-7	5	.118	2.89	N.O.	24.5	150	5	70		Ditto

SUMMARY OF SQUARE PAN TESTS

HALON 1211

(Continued)

Test No.	Fire Size Sq. Ft.	Rate Lb./Sec.	Agent Used, Lb.	Extinguishing Time, Seconds	Application Time, Seconds	N ₂ psig.	Wind mph.	Temp. °F.	Orifice Size	Remarks
02269										
-1	10	.43	11.06	25.6	25.8	150	2	20	3/32"	Reflashing
-2	10	.42	3.56	8.1	8.5	150	2	20	3/32"	
-3	10	.233	4.81	N.O.	20.7	150	2	20	5/64"	
-4	10	.54	7.44	13.1	13.7	150	2	20	7/64"	Reflash
-5	10	.52	10.44	19.2	20.0	150	2	20	7/64"	
-6	10	.614	3.56	5.6	5.8	150	2	20	1/8"	
-8	5	.168	3.97	N.O.	23.6	150	2	20	1/16"	Almost out
04309										
-1	10	.65	9.38	12.5	14.4	150	5	60	1/8"	Pattern too long (15 ft.)
05019										
-1	10	.525	11.63	N.O.	22.2	150	2	65	1/8"	Almost out
-2	10	.60	8.25	13.0	13.8	150	2	65	1/8"	
05049										
-2	10	.85	3.75	4.2	4.4	150	2	65	5/32"	
06119										
-4	10	1.25	4.38	3.3	3.5	125	6	85		Army 50 lb. nozzle modified

SUMMARY OF SQUARE PAN TESTS

HAION 1301

Test No.	Fire Size Sq. Ft.	Rate Lb./ Sec.	Agent Used, Lb.	Extinguishing Time, Seconds	Applica- tion Time, Seconds	N ₂ psig.	Wind mph.	Temp. °F.	Orifice Size	Remarks
10158										
-1	3	.074	.61	7.5	8.3	225	3	70	1/64"	1" D x 3" horn in all tests
-2	4	.063	1.31	N.O.	21.0	225	3	70	1/64"	Reflashing
-3	4	.065	1.31	19.7	20.3	225	3	70	1/64"	Reflashing, limit fire
-4	3	.109	1.31	11.6	12.0	225	3	70	1/32"	
-5	3	.312	.5	1.3	1.6	225	3	70	3/64"	
-6	4	.23	1.22	5.0	5.3	225	6	70	3/64"	
-7	5	.20	4.22	N.O.	21.0	225	6	70	3/64"	
-8	5	.283	1.19	4.1	4.2	320	6	70	3/64"	
-9	6	.29	5.25	17.5	18.1	320	10	70	3/64"	Reflashing, wind giving dif-
-10	6	.28	5.75	N.O.	20.5	300	12	70	3/64"	Ditto
-11	6	.303	1.49	4.3	4.9	400	15	70	3/64"	"
-12	7	.316	6.5	N.O.	20.6	400	15	70	3/64"	"
-13	7	.562	2.81	4.1	5.0	400	10	70	3/32"	"
-14	10	.563	10.5	18.0	18.2	400	12	70	3/32"	Reflashing, limit fire
10178										
-1	10	.564	6.79	11.5	12.0	400	2	55	3/32"	
-3	10	.748	5.47	6.6	7.3	400	2	55	7/64"	
02199										
-1	5	.85	2.12	1.6	2.5	300	10	10	1/8"	
-2	5	.53	1.22	1.7	2.3	300	10	10	3/64"	
-4	5	.225	1.69	6.8	7.5	300	10	10	1/64"	Limit fire
-5	5	.166	3.31	N.O.	20.0	300	10	10	1/64"	

SUMMARY OF SQUARE PAN TESTS

HALON 1301

(Continued)

Test No.	Fire Size Sq. Ft.	Rate Ib./Sec.	Agent Used, Ib.	Extinguishing Time, Seconds	Application Time, Seconds	N ₂ psig.	Wind Mph.	Temp. °F.	Orifice Size	Remarks
02259										
-1	5	.493	1.97	3.7	4.0	300	5	20	3/64"	
-3	5	.267	1.36	4.3	5.1	300	5	20	1/32"	
-4	5	.247	1.24	4.5	5.0	300	5	20	1/64"	
-5	5	.10	2.16	N.O.	21.5	300	5	20	1/64"	
-6	10	.70	3.16	4.4	4.5	300	5	20	7/64"	
-7	10	.508	2.69	5.0	5.3	300	5	20	3/32"	
-8	10	.359	6.75	18.2	18.8	300	5	20	5/64"	Limit fire
-9	10	.404	8.97	N.O.	22.2	300	5	20	5/64"	

SUMMARY OF SQUARE PAN TESTSHALON 2402

Test No.	Fire Size Sq. Ft.	Rate Ib./Sec.	Agent Used, Ib.	Extinguishing Time, Seconds	Application Time, Seconds	N ₂ Psig.	Wind mph.	Temp. °F.	Orifice Size	Remarks
11058										
-1	3	.268	.94	2.5	3.5	250	5	55	1/16"	
-2	3	.355	.92	2.4	2.6	250	5	55	1/16"	
-3	3	.094	.47	4.6	5.0	250	5	55	1/32"	Reflash
-4	3	.082	2.0	N.O.	24.4	250	5	55	1/64"	
-5	5	.122	2.44	N.O.	20.0	250	5	55	3/64"	
-6	5	.252	1.52	5.3	6.0	250	5	55	1/16"	
-7	5	.313	2.0	6.1	6.4	250	5	55	5/64"	Reflash
-8	5	.51	3.17	5.6	6.1	250	5	55	3/32"	
11078										
-1	7	1.34	4.44	2.6	3.3	250	2	42	5/64"	Orifice loose, rate too high
-2	7	.31	1.86	5.5	6.0	250	2	42	5/64"	
-3	7	.226	5.31	N.O.	23.5	250	2	42	1/16"	Reflash
-4	7	.51	3.89	7.3	7.6	250	2	42	3/32"	Pattern too near straight stream
-5	7	.526	3.0	5.2	5.7	250	2	42	3/32"	
-6	10	.508	7.61	14.2	15.0	250	2	42	3/32"	Limit fire
-7	10	.60	7.09	11.2	11.8	250	2	42	7/64"	Reflash
-8	10	.85	2.55	2.5	3.0	250	2	42	1/8"	

NOTE: All orifices had a 60 mesh screen placed 1/16" downstream to form a disperse conical pattern. Otherwise a straight stream was obtained.

50 SQUARE FOOT SPILL FIRES

Test No.	Halon No.	Rate Lb./Sec.	Agent Used, Lbs.	Extinguishing Time, Seconds	Application Time, Seconds	N ₂ psig.	Wind mph.	Temp. °F.	Remarks
05079									
-9	1211	1.11	23.25	21.	21.	150	15	45	3 reflashes--poor pattern--straight stream.
-10	1211	1.25	5.5	4.2	4.4	150	15	45	Wider conical pattern
05129									
-1	1211	1.13	4.75	3.4	4.2	150	5	70	Ditto
-2	1211	.80	10.375	12.5	13.0	150	5	70	2 reflashes--limiting rate
-4	(1211)	.97	4.375	4.1	4.5	175	5	70	No reflash (mixture is 80 weight per cent 1211)
-5	(1211)	.86	3.875	4.3	4.5	175	5	70	Limit rate--one small reflash
05219									
-2	(1211)	.815	3.75	4.6	4.6	125	3	75	Limit rate
05289									
-1	1301	1.1	7.125	6.4	6.5	400	8	70	Army 50 lb. nozzle--insufficient range
-2	1011	1.38	14.5	10.5	10.5	200	8	70	Fan spray--not enough range.
-3	1011	1.03	6.0	4.9	5.8	200	8	70	Ditto
-4	1011	.77	5.0	6.5	6.5	200	8	70	"
-5	1011	.774	8.75	10.6	11.3	200	8	70	" --2 reflashes
-8	1301	1.02	11.25	10.7	11.0	400	5	80	Reflash, Army 50 lb. nozzle
-9	1011	1.02	7.5	7.0	7.2	200	5	80	Fan spray
-10	1211	1.81	12.125	6.4	6.7	300	5	80	Army 50 lb. nozzle--rate too high--weeping
-11	1211	1.61	11.125	6.8	6.9	200	5	80	Ditto
-12	1211	1.19	5.25	3.8	4.4	250	5	80	7/32" orifice, 2.5" D. x 9" horn, better range.
-13	1211	1.19	4.875	3.8	4.1	250	5	80	3/16" orifice, Ditto
-14	1211	1.01	3.25	2.9	3.2	250	5	80	5/32" orifice, Ditto

50 SQUARE FOOT SPILL FIRES

(Continued)

Test No.	Halon No.	Rate Lb./Sec.	Agent Used, Lbs.	Extinguishing Time, Seconds	Application Time, Seconds	N ₂ psig.	Wind mph.	Temp. °F.	Remarks
06089									
-1	1301	1.08	5.375	4.7	5.0	450	10	90	Army 50 lb. nozzle--insufficient range
-2	1011	1.08	5.75	5.3	5.3	200	10	90	Fan spray--insufficient range
-4	1211	1.13	3.625	3.3	3.2	250	10	90	3/16" orifice, 2.5" D. x 9" horn, better range
06099									
-3	1301	1.17	7.5	5.9	6.4	525	10	95	Limit rate--almost reflashed
-4	1011	1.09	8.375	7.2	7.7	250	10	95	No reflash but need more range--fan spray
06119									
-1	1211	1.3	6.50	5.5	5.0	225	6	85	Modified Army nozzle, 5/32" orifice
06099									
-13	(1211 1202)	1.0	7.0	7.8	7.0	225	10	95	Modified Army nozzle, 5/32" orifice (Mixture is 80 weight per cent 1211)

50 SQUARE FOOT FIRES
CONTAINING SIMULATED WING SECTION

Test No.	Halon No.	Rate lb./Sec.	Agent Used, Lbs.	Extinguishing Time, Seconds	Application Time, Seconds	N ₂ psig.	Wind mph.	Temp. °F.	Remarks
06089									
-5	1211	.83	6.875	N.O.	8.3	200	10	90	Insufficient rate. Supporting brick is a flame holder.
-6	1211	.89	6.5	N.O.	7.3	200	10	90	Ditto
-7	1211	.935	10.25	7.4	10.9	200	10	90	Thought extinguishment was secured at 7.4 seconds--reflash
-8	1211	.965	14.25	N.O.	14.8	200	10	90	Insufficient rate--reflash
-9	1011	1.09	10.25	9.5	9.4	200	10	90	Fan spray
-10	1301	1.06	5.0	4.7	4.7	400	10	90	Army 50 lb. nozzle
06099									
-1	1301	.88	11.625	N.O.	13.25	450	10	95	Army 50 lb. nozzle--insufficient rate
-2	1301	1.19	5.5	4.3	4.6	525	10	95	Army 50 lb. nozzle--good rate
-5	1011	1.13	17.0	N.O.	15.0	250	10	95	Fan spray, insufficient rate
-6	1211	1.01	15.875	15.5	15.6	225	10	95	Limit fire
-8	1211	1.31	8.375	6.5	6.4	225	10	95	Army 50 lb. nozzle, X.S. rate
-9	1211	1.03	5.25	5.3	5.1	225	10	95	Modified Army nozzle, 3/16" orifice
06119									
-2	1211	1.15	7.25	6.3	6.3	225	6	85	Modified Army nozzle, 3/16" orifice

SPILLING FUEL FIRES

See Figure 18

5 Gallon Fuel, 20 Second Preburn

Test No.	Halon No.	Rate Lb./ Sec.	Agent Used, Lbs.	Extinguishing Time, Seconds	Application Time, Seconds	N ₂ psig.	Wind mph.	Temp. °F.	Remarks
05289									
-6	1011	.74	8.75	N.O.	11.8	200	8	70	Essentially no effect on fire--rate too low
-7	1011	1.21	20.5	N.O.	16.9	200	8	70	Held intensity down--could not extinguish
06099									
-10	1211	1.24	17.25	14.2	13.9	225	8	95	Army nozzle--improper technique
-12	1211	1.53	11.5	7.1	7.5	225	8	95	Army nozzle--better technique
-14	1211	1.14	7.75	6.6	6.8	225	8	95	Ditto
06119									
-3	1211	1.3	9.1	6.3	7.0	225	6	85	Army nozzle
07139									
-1	1301	1.07	12.0	N.O.	11.2	450	5	80	Army nozzle, reflashing
-2	1301	1.05	7.25	6.8	6.9	450	5	80	Army nozzle.
-3	1301	1.03	8.875	N.O.	8.6	450	5	80	Army nozzle, reflashing

APPENDIX VI

SUMMARY OF EXPOSURE OF RATS AND GUINEA PIGS TO ATMOSPHERES CONTAINING HALON 1211 (CBrClF₂)

Calculated Concentration in Air, % 26-28	Concentration Recovered by Combustion Analysis, %	Duration of Exposure in Hours 0.7	Animals Exposed		Number Killed Number Exposed 4/4	Results, Observations and Comments
			Male Rats	Female Guinea Pigs		
26-28	23	0.5	Male Rats 2/4	Female Guinea Pigs 1/8		Immediate tremors. Convulsions in about 4 min. One rat died after 5-6 min. exposure. Several dead after 24 min. of exposure. All dead after 42 min. One rat dead after 20 min. Second rat dead on removal. Survivors lost only a small amount of weight which they had more than regain in 6 days. One guinea pig was dead on removal. Survivors required over 2 weeks to regain weight loss.
26-28	23	0.25	Male Rats 0/8	Female Guinea Pigs 0/8		Convulsions and severe tremors started after about 1 min. The rats stayed in this condition until the exposure ended. They went through the classic stages of anesthesia and recovered quickly (5-10 min.). Only one rat lost any weight and he recovered quickly.
26-28		0.25	Male & Female Guinea Pigs 1/4			The guinea pigs responded almost immediately by blinking their eyes. This was followed shortly by twitching of the ears and jerking which be- gan after about 1 min. Convulsions started about 20 sec. later. The respiratory rate con- tinued to increase during the entire exposure. All were alive on removal and were able to walk in about 5-10 min. after having gone through the various stages of anesthesia while recovering consciousness. One guinea pig died 10 days after exposure, possibly due to extraneous causes.

SUMMARY OF EXPOSURE OF RATS AND GUINEA PIGS TO
ATMOSPHERES CONTAINING HALON 1211 (CBrClF₂)

(Continued)

Calculated Concentration in Air, %	Concentration Recovered by Combustion Analysis, %	Duration of Exposure in Hours	Animals Exposed	Number Killed	Number Exposed	Results, Observations and Comments
17	16	7.0	Male Rats	3/4		All rats became unconscious during the first few minutes of exposure and remained unconscious during the rest of the exposure. First rat died after 2.5 hrs. exposure. Two more died after 5 hrs. On removal, the surviving rat was unconscious and breathing very slowly. The pupil of his eyes were dilated. He did not recover appreciably in 10 min. but appeared normal the next day. The animal lost weight and did not regain it until after 1 wk.
17		2.0	Male Rats	2/8		Two rats died after about 1.5 hr. exposure. Rats would respond to tapping on jar. Weight loss was minor and recovered quickly.
		1.4	Male Guinea Pigs	4/4		Dead on removal.
		1.0	Male & Female Rats	0/8		Severe tremors but could still respond to tapping after 1 hr. Quickly regained weight.
		1.0	Male Guinea Pigs	0/8		Moderate weight loss, regained in 1 week.

17 NOTE: An additional group of 4 guinea pigs was exposed for 1 hr. Because one animal died 1/2 hr. after exposure, it and the other 3 guinea pigs were sacrificed for signs of pathological changes. The death of the one pig could not be attributed to the exposure as generally hemorrhages of the stomach, intestines, spleen, coronaries of the heart were found. A second guinea pig sacrificed at the same time, as well as one sacrificed on the second day and on the ninth day, had only slight hemorrhages of the lung with no other gross pathological symptoms.

SUMMARY OF EXPOSURE OF RATS AND GUINEA PIGS TO
ATMOSPHERES CONTAINING HALON 1211 (CBRC1F₂)

(Continued)

Calculated Concentration in Air, %	Concentration Recovered by Combustion Analysis, %	Duration of Exposure in Hours	Animals Exposed	Number Killed Number Exposed	Results, Observations and Comments
9.4	8.3 to 8.4	6.5	Male & Female Rats	0/8	Rats were very slow moving but occasionally changed position. They recovered quickly after the exposure.
9.4	8.3	6.5	Guinea Pigs	2/8	Guinea pigs moved staggeringly, apparently more affected than the rats receiving the exposure at the same time. Recovered quickly after exposure and were able to walk in a few minutes. Six animals had more than recovered their weight in 1 wk. One animal died 10 days after exposure. One animal was sacrificed 5 days and death only questionably related to exposure.
9.4	NOTE: Additional groups of 5 rats and 5 guinea pigs were exposed for 7 hrs. One rat and one guinea pig were sacrificed each day for 5 consecutive days. No consistent pathology was noted which could be attributed to the exposure.				
9.4		4.		0/8	All animals regained weight rapidly.

SUMMARY OF EXPOSURE OF GUINEA PIGS TO
ATMOSPHERES CONTAINING HALON 1301 (CBrF₃)

<u>Calculated</u> <u>Concentra-</u> <u>tion in</u> <u>Air, %</u>	<u>Concentration</u> <u>Recovered by</u> <u>Combustion</u> <u>Analysis, %</u>	<u>Duration</u> <u>of</u> <u>Exposure</u> <u>in Hours</u>	<u>Animals</u> <u>Exposed</u>	<u>Number</u> <u>Killed</u> <u>Number</u> <u>Exposed</u>	<u>Results, Observations and Comments</u>
37	28 to 42	7.0	Female Guinea Pigs	0/12	All animals showed obvious signs of difficulty in breathing. Within 5 min. guinea pigs were slow moving but would respond to tapping on the jar. After 8 min. exposure, the animals started jerking and continued to jerk throughout exposure. The oxygen concentration was measured by a portable Bacharach oxygen meter and was found to range from 11 to 13%. Two guinea pigs sacrificed 10 and 12 days after exposure and only normal pathology.

NOTE: In view of the lack of physiological effect of the agent at this concentration, no higher concentrations were studied because the lowering of the oxygen content was becoming important.

SUMMARY OF ACUTE EXPOSURES OF RATS AND GUINEA PIGS

TO HALON 2402 (C₂Br₂F₄)

Calculated Concentration in Air, %	Concentration Recovered by Combustion Analysis, %	Duration of Exposure in Hours	Animals Exposed	Number Killed Number Exposed	Results, Observations and Comments
12		0.2	Male Guinea Pigs & Male Rats	1/8 8/8	Rats and guinea pigs were exposed simultaneously. Rats were unconscious in 2 min., guinea pigs staggering. After 3 min., 3 rats were dead and guinea pigs convulsing. All rats were dead at 6 min. Died quietly. Guinea pigs continued to convulse severely until the exposure was over. Five min. after removal from exposure, 2 guinea pigs were trying to stand. There was a rather rapid recovery of consciousness.
6		3.0	Male Rats & Male Guinea Pigs	4/8 2/8	Rats and guinea pigs were exposed simultaneously. Rats started to stagger and fall immediately. Within 5 min., rats were lying on their sides unable to get up. One rat died after 40 min., another at 100 min. Four rats were dead on removal. Survivors lost a small amount of weight and recovered quickly. Two rats were examined 16 days after exposure and no gross pathological changes seen. Guinea pigs were much less severely affected but suffered severe tremoring and convulsions during the entire exposure. All the guinea pigs were alive after 2 hrs. exposure but 2 were dead after 3 hrs. The survivors lost a small amount of weight but recovered quickly. Two guinea pigs were sacrificed 16 days after exposure and slight to moderate kidney pathology was noted.

SUMMARY OF ACUTE EXPOSURES OF RATS AND GUINEA PIGS

TO HALON 2402 (C₂Br₂F₄)

(Continued)

Calculated Concentration in Air, %	Concentration Recovered by Combustion Analysis, %	Duration of Exposure in Hours	Animals Exposed	Number Killed	Number Exposed	Results, Observations and Comments
6		1.0	Male Rats & Guinea Pigs	0/8	0/8	Similar responses as above. Two rats and 2 guinea pigs were sacrificed 16 days after exposure. The rats were normal but one cavy had very slight changes evident in the kidneys on gross observation.
3	3-4	7.0	Male Rats & Guinea Pigs	1/8	0/8	Rats became unconscious after one hr., all were alive at end of the exposure. All lost a small amount of weight but apparently all but one quickly recovered. One rat died 16 days after exposure after losing weight during the entire period. He was not necropsied but 2 survivors were killed at this time and were normal in gross pathology. Guinea pigs were unconscious after one hr. and severe convulsions while recovering unconsciousness. The guinea pigs were slow moving the next day but apparently all recovered satisfactorily. Two guinea pigs were sacrificed 18 days after exposure and moderate pathology of the kidneys was seen.
1		7.0	Male Rats & Guinea Pigs	0/8	0/8	Rats were less active than normal during exposure. All were alive on removal. All rats lost a small amount of weight but generally recovered in 1 wk. Two rats were sacrificed 21 days after exposure and slight liver and slight kidney pathology noted. Guinea pigs did not appear to be affected by the exposure.

SUMMARY OF EXPOSURE OF RATS AND GUINEA PIGS TO
ATMOSPHERES CONTAINING HALON 1202 (CBr₂F₂)

Calculated Concentration in Air, %	Concentration Recovered by Combustion Analysis, %	Duration of Exposure in Hours	Animals Exposed	Number Killed	Number Exposed	Results, Observations and Comments
7.4	6.4-6.7	0.5	Female Rats	8/8		All animals died quietly in the last 5 min. of exposure after severe convulsions and tremors.
7.4		0.4	Male Guinea Pigs	8/8		Six guinea pigs died during last 4 min. of exposure. Two animals were alive after the exposure but lost weight and died in one week or less.
7.4		0.2	Female Rats	2/8		Severe convulsions immediately after exposure started. One rat died in 4.5 min. and the second in 10 min.
7.4-8		0.2	Male Guinea Pigs	0/8		Severe tremors.
7.4		0.1	Female Rats	1/8		Rat was dead on removal. Severe tremors all during exposure. Animals did not lose any weight after exposure.
4.0		4.0	Female Rats	4/4		Severe tremors. Two were dead on removal. One died while being removed from exposure. The fourth died 2 hrs. after exposure.
4.0		3.0	Male Guinea Pigs	3/4		One death during exposure. One death 3 days later. One death 20 days later.
4.0	3.2	2.0	Female Rats	5/12		One death at 20 min. Four dead on removal. Survivors lost a slight amount of weight.
4.0		2.0	Male Guinea Pigs	3/4		Two deaths after 1 hr. One death 5 days later.

SUMMARY OF EXPOSURE OF RATS AND GUINEA PIGS TO
ATMOSPHERES CONTAINING HALON 1202 (CBr₂F₂)

(Continued)

Calculated Concentra- tion in Air, %	Concentration Recovered by Combustion Analysis, %	Duration of Exposure in Hours	Animals Exposed	Number Killed Number Exposed	Results, Observations and Comments
4.0		1.0	Female Rats	0/8	Tremors occurred after 1 min. These continued during the entire exposure. Only very slight loss of weight occurred.
4.0		1.0	Male Guinea Pigs	0/8	Tremors and convulsions started immediately and continued during the exposure. Two guinea pigs were sacrificed for pathological examination 3 and 4 days after exposure. Acute pneumonia and lung congestion were found.
2.0		7.0	Male & Female Rats	4/8	Severe convulsions and tremors. Three rats died next day. The other rat was sacrificed on 2nd day in moribund condition with severe tremors. Moderate lung and kidney pathology were seen.
2.0		7.0	Male Guinea Pigs	5/5	Immediate tremors, four dead on removal, one dead the following day.
2.0	2.1	4.0	Female Rats	0/8	Slight to moderate weight loss.
2.0		4.0	Male Guinea Pigs	0/8	Tremors during exposure. Weak the next day.

SUMMARY OF ACUTE EXPOSURES OF RATS AND GUINEA PIGS TO
ATMOSPHERES CONTAINING HALON 1011 (CH₂BrCl)

Calculated Concentration in Air, %	Concentration Recovered by Combustion Analysis, %	Duration of Exposure in Hours	Animals Exposed	Number Killed Number Exposed	Results, Observations and Comments
8		0.2	Male & Female Rats	10/10 10/10	All animals were dead at the end of the exposure.
8		0.1	Male & Female Rats	0/10 0/10	There was excessive salivation. All animals were unconscious upon removal. Recovered consciousness rather slowly. Little or no weight loss.
4		0.4	Male & Female Rats	10/10 10/10	Death was due to anesthesia. Rats were blue in color (cyanotic). Abdominal breathing was seen.
4		0.2	Male & Female Rats	3/10 3/10	Rats died within five minutes after the termination of exposure.
4		0.1	Male & Female Rats	0/15 0/15	Unconscious on removal. Recovered rapidly. Slight lung pathology and fatty infiltration of the liver were noted. No fibrotic changes were seen in the liver.
2		1.5	Male Guinea Pigs	5/5	Anesthetic effects were noted in less than one minute. One guinea pig was dead after 48 min. Two dead after 71 min. The other 3 were alive on removal but died over night.
2		1.0	Male & Female Rats	9/10 6/10	Fourteen were dead at the end of the exposure. One died 6 days later.
2	1.68	0.5	Male Guinea Pigs	0/5	

SUMMARY OF ACUTE EXPOSURES OR RATS AND GUINEA PIGS TO
ATMOSPHERES CONTAINING HALON 1011 (CH₂BrCl)

(Continued)

<u>Calculated</u> <u>Concentration in</u> <u>Air, %</u>	<u>Concentration</u> <u>Recovered by</u> <u>Combustion</u> <u>Analysis, %</u>	<u>Duration</u> <u>of</u> <u>Exposure</u> <u>in Hours</u>	<u>Animals</u> <u>Exposed</u>	<u>Number</u> <u>Killed</u> <u>Number</u> <u>Exposed</u>	<u>Results, Observations and Comments</u>
2		0.5	Male & Female	1/10 0/10	One rat died after 28 min. exposure, probably due to respiratory failure. All rats were unconscious at the end of the exposure. All animals showed evidence of respiratory difficulty and excessive salivation. Very slight weight loss which was quickly regained.
1	0.88-0.89	2.5	Male Guinea Pig	1/5	Died six days after exposure.
1		2.0	Male Guinea Pigs	0/5	After 27 min., the ear reflexes of the guinea pigs were still operating. The back legs were out of control but were trying to stand on the front legs.
0.5		7.0	Male & Female Rats	0/10 0/10	Marked drowsiness and disturbances of equilibrium, loss of muscle control were apparent. No great depression or excitement. Slight lung pathology and slight fatty changes in the liver were noted.

SUMMARY OF EXPOSURE OF GUINEA PIGS TO
ATMOSPHERES CONTAINING HALON 104 (CCL₄)

<u>Calculated</u> <u>Concentra-</u> <u>tion in</u> <u>Air, %</u>	<u>Concentration</u> <u>Recovered by</u> <u>Combustion</u> <u>Analysis, %</u>	<u>Duration</u> <u>of</u> <u>Exposure</u> <u>in Hours</u>	<u>Animals</u> <u>Exposed</u>	<u>Number</u> <u>Killed</u> <u>Number</u> <u>Exposed</u>	<u>Results, Observations and Comments</u>
2	1.6-1.7	1.0	Male Guinea Pigs	4/5	All guinea pigs were unconscious but alive on removal. Four died 2 days later after appearing sick and losing weight. One animal was autopsied and had a very severely fatty liver. The survivor was sacrificed 12 days after exposure and still had a slightly fatty liver.
2		0.5		0/5	All unconscious on removal.
1		2.0		4/4	One guinea pig died 2-5 days after exposure. One guinea pig was sacrificed after 7 days and still had a severely injured liver.
1		1.5		0/5	Moderate weight loss and prolonged recovery occurred after exposure.

APPENDIX VII

EXPERIMENTAL METHOD FOR ACUTE VAPOR TOXICITY DETERMINATIONS

Exposures were conducted in either a 19 liter glass jar or in 160 liter cubical glass and Monel chambers. In all cases, exposures were to a dynamic concentration with air flows sufficient for the group of animals being exposed. Air flows were maintained by suitable exhaust pumps and were measured by flow meters. Because the high concentration used during some experiments changed the density and viscosity of air considerably, the calibrations of the flow meters for air were not valid. It was, therefore, necessary to use a wet test meter in series with the flow meter in order to establish the actual volume of air flowing per time interval at a particular flow meter setting. Sufficient observations were made in all cases to assure accuracy of air flows well within the limits of the experiment. In all cases, the concentrations were maintained by metering the agents into a mixing flask through which the air was drawn into the exposure vessel. Metering of the agents was done by the means of Dual Syringe Feeder pumps⁷⁰. In some cases, the gas was metered directly from a cylinder by means of calibrated flow meters (Halone 1301 and 1211). When the dual syringe feeder pumps were used to pump gases (Halone 1211 and 1202) the gas supply was held in a 100 liter Saran plastic bag which served as a reservoir. This permitted pumping undiluted gas at room temperature and pressure.

Analysis of the atmosphere in exposure vessels was made by combustion of the air or a secondary dilution of the air in a platinum packed quartz tube at 1000°C. The combustion products were absorbed in 30 milliliters of a 10% sodium formate-1% sodium carbonate solution in water in a beaded glass scrubber and subsequently titrated for the chloride or bromide by a micro Volhard technique.⁷¹ The secondary dilution of the chamber atmosphere was necessitated by the extremely high concentrations used and the thermal stability of some of the compounds. The secondary

dilutions were made by pumping a small volume of air from the exposure vessel into the air stream which passed through the combustion analyzer. This aliquoting of air was done by means of a dual syringe feeder pump.

Dual syringe pumps were also used to meter air to a continuous combustion conductivity analyzer⁷² which was used to monitor most of the exposures. This combustion analyzer was used to reduce the possibility of sudden changes in concentration which might not be detected by periodic samples taken for titration of halide. This made it possible to limit the number of samples taken for titration and still remain certain that exposure levels were close to the desired concentrations. Greater emphasis could thereby be placed on observation of the animal responses rather than on the exposure equipment.

The animals used in these experiments were healthy young adults of suitable weight range and from homogenous stock. The rats were selected from the stock colony of the Biochemical Research Laboratory of The Dow Chemical Company and the guinea pigs were obtained from a commercial breeder⁷³. Animals were weighed before exposure and at intervals after exposure for at least two weeks or, if required, until the animals were growing satisfactorily and had regained their original weight. The animals were observed during the exposure and after the exposure for symptoms of effects on the central nervous system or other untoward effects resulting from the exposure. Some animals were sacrificed and examined for gross pathological changes as indicated in the summary tables. Because several groups of animals were exposed to each concentration, the observations made on one group will generally apply to the other groups exposed to that same concentration. Hence, all observations will not be repeated for each exposure condition.