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AN APPRAISAL OF HALOGENATED FIRE EXTINGUISHING AGENTS. PROCEEDINGS OF A SYMPOSIUM, HELD AT NATIONAL ACADEMY OF SCIENCES, WASHINGTON, D. C. ON APRIL 11-12, 1972

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Symposium on

An Appraisal of Halogenated Fire Extinguishing Agents

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An Appraisal of Halogenated Fire Extinguishing Agents

Proceedings of a Symposium

April 11-12, 1972

held at

National Academy of Sciences
Washington, D.C.

Conducted by

Committee on Fire Research
Division of Engineering
and
Committee on Toxicology
Division of Chemistry and Chemical Technology
of the
National Research Council

NATIONAL ACADEMY OF SCIENCES
Washington, D.C.
1972

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PREFACE

The following Proceedings of the Symposium on "An Appraisal of Halogenated Fire Extinguishing Agents" consist essentially of two groups of papers. One group involves very practical applications described from engineering and fire protection points of view. The other group comprises fundamental toxicity research studies designed to identify any potential health problems. Since the intent of the Symposium was to provide an up-to-date basis for intelligent selection of which, if any, of the halogenated agents should be used in a given set of circumstances, it seems appropriate to provide some perspective on these two groups of papers.

The applications papers describe the effectiveness of the various agents and "how to do it." Their findings are directly applicable to actual fire control situations. The toxicity papers serve to identify what might possibly happen under the worst conceivable circumstances. They also provide insight on safe circumstances of human exposure and on potential problems that might be associated with actual exposure during fire control activities. By their very nature these papers cannot be precisely related to actual fire-fighting activities and thus their interpretation requires professional judgement.

The Symposium clearly shows that the possible health effects in a fire-fighting situation arise from three sources: (a) the fire and its combustion products, (b) the control agent, and (c) its combustion products. The risk to human health and property from (a) and (c) can be kept to a minimum by sensitive and rapid engineering methods for detecting the fire and delivering the agent. The risk to human health from (b), the agent, during fire-fighting requires a judgement of probable effects from the calculated amounts of agent to be used and the estimated time of exposure. The overall assessment of risk to health and property is one of balancing these three considerations. The choice among halogenated agents and between them and some other fire control system is a similar balancing of risk. The Proceedings of the Symposium provide a current state of knowledge upon which to base such judgement. There are many circumstances in which these materials may be safely and effectively used. The choice between agents depends upon the detailed circumstances.

The Symposium also shows quite clearly that the effectiveness of these agents can be markedly affected by the design and operation of the total fire control system. Fires present minimum threat to property or health when they are detected early in their development and extinguished rapidly (less than ten seconds) with sufficient agent. The opposite situation exists with a longstanding fire involving heated metal surfaces when it is attacked by a limited hand-held extinguisher.

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Effectiveness and health hazards are also subject to variation depending on the location of the fire, for example, whether it is in a confined space subject to total flooding or in a windy open area.

The reader is urged to seek knowledgeable advice concerning a particular application when deciding to use any of the halogenated agents.

Herbert E. Stokinger, Chairman
Committee on Toxicology

Carl W. Walter, Chairman
Committee on Fire Research

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I ORIENTATION SESSION

Chairman, William J. Christian

WELCOME AND INTRODUCTION

Carl W. Walter

Harvard Medical School

Dr. Christian: I would like to welcome you all to this Symposium on "An Appraisal of Halogenated Fire Extinguishing Agents" and to introduce to you the Chairman of the Committee on Fire Research, Dr. Carl Walter of Peter Bent Brigham Hospital and Harvard University.

Dr. Walter: A brief word concerning this symposium. As you know, the halons are sort of a special-purpose fire extinguishing agent, and while many still doubt their effectiveness, many realize they are potent agents, particularly in special situations.

There has been much discussion, and many reports concerning toxicity of these agents as they are used. Part of this stems from the fact that there is a wide spectrum of use from accidental dispersal to using them in small quantities on very advanced fires. Hence the toxicology is a spectral sort of experience, and many techniques have been developed to permit the safe use of these agents. It is this kind of information that we hope to review during this symposium, so that everybody understands what we are talking about, and that we can go forward constructively in the application of these spectacular agents in the control of special situations.

I would like to introduce members of the two Committees that sponsored this symposium, so that you know who they are. If you have any questions, feel free to buttonhole them during the course of the symposium.

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REMARKS

Dr. Christian: This first session we have entitled an Orientation Session. We hope here to develop a little background on these agents for some of you who may not be as familiar with the history and development and effectiveness of halogenated agents as many of us are.

The first speaker is my colleague from Underwriters' Laboratories, Stanley Auck. His present position is Associate Manager in the Fire Protection Engineering Department. He has responsibility for fire protection equipment and systems. I think he is, so to speak, in the thick of things with these particular kinds of materials. He will speak on a "Short History of Halogenated Fire Extinguishing Agents."

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SHORT HISTORY OF HALOGENATED FIRE EXTINGUISHING AGENTS

S. E. Auck

Underwriters' Laboratories, Inc.

Before entering a discussion of the history of halogenated fire extinguishing agents, I feel that it is important that the stage be properly set by providing definitions of some of the important terms that will be used in the discussion.

The title of this paper contains two items that might be in need of definition in order to carry out a proper discussion of this topic. The first term I'll consider is that of "fire extinguishing agent." Webster tells us that fire is "the phenomenon of combustion manifested in light, flame, and heat." To extinguish is to "cause to cease burning." And finally, an agent is "something that produces or is capable of producing an effect" (1). So putting this all together, we have "something that is capable of causing the cessation of combustion as manifested in light, flame, and heat."

Still working with the title of the paper, we must next discuss the term "halogenated." Here Webster says that this means treated or caused to combine with a halogen. Since that seems somewhat circular, we must obtain a definition for "halogen." A halogen is one of the elements fluorine, chlorine, bromine, and iodine. There is another element in the group -- astatine -- but this one has not been found in nature. These elements make up Group 7a of the periodic system, and they have been given the name "halogen" which is derived from Greek words meaning "salt former" (2).

There are thousands upon thousands of halogenated compounds, but since we are interested in those halogenated compounds that are or have been used as fire extinguishing agents, the field is drastically narrowed. I would imagine that there are no more than two dozen halogenated compounds in existence that could be effectively used for extinguishing fires, and of these there are only about six that have ever been used in significant quantities. These are Halons 104 (carbon tetrachloride), 1011 (chloro bromomethane), 1001 (methyl bromide), 1301 (bromo trifluoromethane), 1211 (bromochlorodifluoromethane), and 2402 (dibromotetrafluoroethane). Of these six, only the first four have been commercially significant in this country.

Now to the history of these agents. At the turn of this century, fire extinguishers generally fell into one of two groups, e.g. soda-acid extinguishers or fire buckets filled with water. These

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devices were suitable for use on fires requiring cooling and quenching for extinguishment, but were of little value on fires involving flammable liquids. This situation was a matter of concern to a great many people because the industrial revolution, which was in full swing at this time, was bringing with it the increased use of combustible lubricants and flammable liquids. The rapidly increasing popularity of the automobile and the advent of the airplane created widely dispersed uses of highly flammable gasoline.

Sometime in the interval of 1902 to 1908, the first halogenated agent extinguishers were developed. In 1911, the first tested halogenated agent extinguisher appeared on the fire protection scene (3). This latter device was a small, pump-type portable fire extinguisher which used as an extinguishing agent a fluid that was principally carbon tetrachloride (Halon 104).

Evaluations of this extinguisher by testing organizations noted that "these devices were found efficient on incipient fires in materials where water or solutions containing large percentages of water are not effective." They were also found "to be effective in extinguishing fires involving electrical arcs of considerable capacity, fires in limited quantities of volatile liquids, fires in calcium carbide, and incipient surface fires on materials which absorb and retain the liquid and retard its volatilization." These characteristics enabled the public to avail themselves of an extinguisher for combatting types of fires which they had previously been unable to handle.

What was this new agent that had been discovered? The fact of the matter is that carbon tetrachloride was not new, having been discovered in 1839 (4). In 1847 it had been used as an anesthetic for medical operations, but was discarded because "the boundary between insensibility and death appears to be so narrow and ill-defined as in practice not to be capable of regulation" (5). The material had also been used in England about 1900 as a dry shampoo although this use seems to have ceased sometime around 1913. With the advantages this material had for extinguishing fires, it seemed like an excellent agent.

By 1917, there was some discussion going on concerning what effects carbon tetrachloride might have on the human system. At that time, a number of people active in the extinguisher field were saying that this material had only an anesthetic effect and that no toxicological harm would come to persons using such extinguishers. Then in 1918, the tune began to change slightly and it was recognized that there was "some toxic effect" associated with this agent and that care should be taken in using it in confined spaces (3). This warning about confined spaces had been around for some years, but it was originally promulgated on the basis of the nature of the gases generated by the decomposition of the agent as it was used on fires. The year 1919 brought with it the first recorded deaths directly attributed to the use of this type of extinguisher when two men working on the construction of a submarine were killed. One man's clothing had caught on fire and the other man extinguished the fire with a carbon tetra-

chloride agent fire extinguisher. Both were overcome by the fumes and later died (4).

In the twenties, the problem of toxicity of this agent received further consideration by a variety of people, but nothing was really done about it because the advantages of this agent were so great. During this time, another problem with this agent began to appear, that being its corrosiveness. This problem received great attention, as it was felt that additives used in the extinguishing agent compounds were the cause of this problem, and it was possible that a suitable substitute could be found. These additives were used for suppression of the freezing point of the extinguishing agent. Also the impurities that were a part of the basic carbon tetrachloride agent were investigated with a view towards their elimination (3).

In October 1932, Underwriters' Laboratories, Inc. published the first Edition of the Standard for Hand Fire Extinguishers, Vaporizing Liquid Type (Sizes Under One Gallon), UL42A. It was in this era that another halogenated agent made its first appearance on the American scene. This agent was methyl bromide (Halon 1001) and it was introduced as being "the standard of all Europe" as far as vaporizing liquid agents were concerned. This agent was never accepted by any nationally recognized fire extinguisher testing laboratory in this country, but it did find usage for many years in small unapproved extinguishers. This non-acceptance was largely based on a study conducted by Underwriters' Laboratories, Inc. in 1932 which was reported on in that year under the title of "The Comparative Life, Fire, and Explosion Hazards of Common Refrigerants" (6). The materials tested in this study included methyl bromide and carbon tetrachloride, and one of the results of the study was the establishment of a toxicity grading scale. The tests showed that methyl bromide was more toxic than carbon tetrachloride, and to use such an agent was considered to be a step in the wrong direction (3).

Through the thirties, the toxicity of vaporizing liquid extinguishants continued to be a problem. But the use of these materials continued to grow because there was no better substitute. During this era, methyl bromide was often used as a fumigant for foodstuffs such as cheese and nuts. The use of carbon tetrachloride in numerous unapproved glass bulb extinguishers was noted. The corrosion problem didn't let up either. Numerous reports of one- or two-year-old extinguishers being inoperable because of corrosion continued to come to light.

With the coming forties, the world went to war, and the halogenated agents went along, too. The use of carbon tetrachloride extinguishers expanded rapidly with the expansion of our war effort. The "other side" did a similar expansion, and, as a matter of fact, it was the Germans who are generally given credit for the development of the next major advance in halogenated agents. During the war, they had found that chlorobromomethane (Halon 1011) was an effective fire fighting agent. With the defeat of Germany in 1945, this information became available to this country, and by 1946, a number of firms began to test extinguishers using this material. In 1947, Underwriters' Laboratories, Inc. issued a report on the material entitled "The Life

Hazards and Nature of the Products Formed When Chlorobromomethane Extinguisher Liquid is Applied to Fires" (7). The report generally showed that this material could be considered to be on a toxicity level comparable with carbon tetrachloride, but it was a more efficient fire extinguishing agent than carbon tetrachloride. It was found that the same general kind of products of decomposition were formed by both materials. In the late 1940's, approved extinguishers using this material became available. It was in this era of the mid-1940's that sales of approved types of these vaporizing liquid type extinguishers reached a peak with about one and a half million units being sold per year. 1950 brought with it a number of important events. Another Halon compound was being introduced in fire extinguishing work with the testing at the Fort Belvoir military test facility of units containing Halon 1301. The use of this particular Halon represented an important departure from past practice in that this was the first fire extinguishing Halon to have a boiling point below $0^{o}C$ (8). For this reason, extinguishers using this material were not classified as vaporizing liquid types but were instead referred to as liquified gas types. By 1954, this material and another newcomer, Halon 1211, had been tested for toxicity and it was found that in their natural state they were appreciably less toxic than Halons 104, 1011, and 1001. Preliminary indications also indicated that these materials would not be subject to the corrosion problems that had plagued halogenated fire extinguishing agents in the past.

The late 1950's could best be classified as the beginning of the end for carbon tetrachloride as a fire extinguishing agent. The rising popularity of dry chemical fire extinguishers, which had no toxicity problem and greater efficiency besides, had brought sales levels down to a fraction of what they had been in 1945. And the toxicity problem had reached the point where at least two states had passed laws prohibiting the use of carbon tetrachloride in fire extinguishers (4).

The 1960's brought about the official death of one halogenated fire extinguishing agent, and an almost universal acceptance of another. In 1962, the 1301 extinguisher became "approved" by nationally recognized testing laboratories, with the result that sales of this type of extinguisher began a long, slow rise. And the "band wagon" to outlaw carbon tetrachloride really went into high gear. Throughout this decade, individual states and municipalities were passing laws and ordnances outlawing the use of this material. In 1966, Underwriters' Laboratories of Canada proposed the elimination of all halogenated fire extinguishing agents on the basis of toxicity in the natural state and toxicity of the products of decomposition. This proposal was later modified to allow continued recognition of 1301, but by March of 1967, ULC had withdrawn all recognition of all other halogenated fire extinguishing agents. In 1966, Underwriters' Laboratories, Inc. proposed to withdraw recognition of those agents having a natural state toxicity of Group 4 or lower. This grouping refers to the toxicity scale developed as part of the work done in the 1930's that was mentioned earlier. The net effect was to drop recognition of Halons 104, 1011 and 1001. After much discussion and a careful study of the problem, this action became final on June 1, 1968.

In early 1968, the federal government entered the picture by proposing to ban the interstate shipment of carbon tetrachloride under the provisions of the Hazardous Substances Act. Again, there was a restudy of the problem, complete with public hearings, and on March 3, 1970, this proposal became the law of the land. These actions created an intensified interest in Halon 1301, especially where a fixed "clean agent" extinguishing system was needed.

The 1970's opened as a decade of promise for Halon 1301. Acceptance of the material as used in portable fire extinguishers was continuing to grow. In the area of fixed systems, the use of the material had really begun to "take off," with a number of manufacturers entering the field with systems for total flooding of hazard spaces. Recently, we have seen the introduction into this country of the use of Halons 1211 and 2402. Both of these materials have been successfully used in many European countries for some years in both portable extinguishers and fixed systems (9).

That brings us to the present, and one might ask, "Where do we go from here?" I'm not one for doing much in the way of "crystal ball" forecasting, but I think that certain things can be said about the immediate future of halogenated fire extinguishing agents. First, Halon 1301 is clearly established as being a useable fire extinguishing agent for a number of reasons, and its use will grow rapidly. It is a "clean" agent, leaving no residue behind after its use. It is relatively nontoxic in its natural state, and it is fairly efficient in extinguishing fires. For Halons 1211 and 2402, the "crystal ball" becomes somewhat cloudy. The former will find some application in portable fire extinguishers in this country, and its use in fixed systems will probably also come about. With Halon 2402, I just don't know what will happen. I do know that for both of these materials, there have been and will continue to be considerable investigations into their respective toxicities. This concern about toxicity is based on the fact that we no longer need accept high toxicity in order to be able to extinguish fires, and we don't want to repeat the history of carbon tetrachloride.

REFERENCES:

1. P. B. Gove, "Webster's Seventh New Collegiate Dictionary," G. & C. Merriam Co., Springfield, Mass., 1967.

2. H. H. Sisler, C. A. Vander Werf and A. W. Davidson, "General Chemistry - A Systematic Approach," pp. 398-418, The Macmillan Co., New York, N. Y., 1954.

3. Underwriters' Laboratories, Inc., "Subject 42 - Extinguishers, Vaporizing Liquid," Chicago, Ill., Unpublished.

4. W. A. Schmidt, "Hazards of Carbon Tetrachloride Fire Extinguishers - Recommended Practices Number 3," pp. 1-5, Federal Fire Council, Washington, D. C., 1967.

5. T. Nunneley, "The Tetrachloride of Carbon as an Anesthetic," British Medical Journal, 1:685, 1867.

6. A. H. Nuckolls, "The Comparative Life, Fire and Explosion Hazards of Common Refrigerants," Underwriters' Laboratories, Inc., Chicago, Ill., 1933.

7. A. F. Matson and R. E. Dufour, "The Life Hazards and Nature of the Products Formed When Chlorobromomethane Extinguisher Liquid is Applied to Fires," Underwriters' Laboratories, Inc., Chicago, Ill., 1948.

8. R. C. Weast, "Handbook of Chemistry and Physics," pp. C-404 to C-407, The Chemical Rubber Co., Cleveland, Ohio, Forty-Sixth Edition, 1965.

9. Underwriters' Laboratories, Inc., "Subject 1058 - Halogenated Agent Extinguishing System Units," Chicago, Ill., Unpublished.

REMARKS

Dr. Christian: I am going to assume that there will be no discussion on that paper since we are just about on schedule.

As the Committees approached setting up this symposium, it became clear to us rather quickly that to keep the thing within bounds of time, we would not be able to say an awful lot about the comparison of halogenated agents with other kinds of fire extinguishing agents. Yet you can hardly go through this thing without some comparison, I think. In order to get that established rather early in the program, I asked the next speaker if he could give us a capsule summary of effectiveness of these agents as opposed to other extinguishants which have been used, to give us an idea of why there is any interest at all in halogenated agents, and why we should be considering them.

The next speaker is a member of the firm of Rolf Jensen and Associates, consulting fire protection engineers. He has been in the fire extinguishing business for more years than he would care for me to mention, I think, previously having been associated with the Ansul Company. I would like to present to you Mr. Merritt Bauman who will speak on the "Comparative Effectiveness of Halogenated Agents and Other Extinguishants."

COMPARATIVE EFFECTIVENESS OF HALOGENATED AGENTS AND OTHER EXTINGUISHANTS

Merritt R. Bauman

Rolf Jensen and Associates, Inc.

Webster defines effectiveness as "a measure of the ability to accomplish a purpose." In the fire protection fraternity we tend to measure the effectiveness of an agent or system on the basis of either its ability to cope with a specific hazard or a relative difference between different agents or systems. In either case, it is akin to answering that old vaudeville question, "How's your wife?" with "Compared to what?"

To identify the absolute and relative effectiveness of halons and other extinguishants, let's start with a definition of terms.

Figure 1 illustrates the interplay by which products are developed and brought to the marketplace under the codes and standards that control or influence their design and use.

The scientist in the research area is doing either theoretical work to identify the mechanism of extinguishment or applied research to evaluate candidate agents in small bench top tests. Most of the effectiveness measurements he makes are based on per cent volume, weight, or molal concentrations. Research is the acquisition of knowledge.

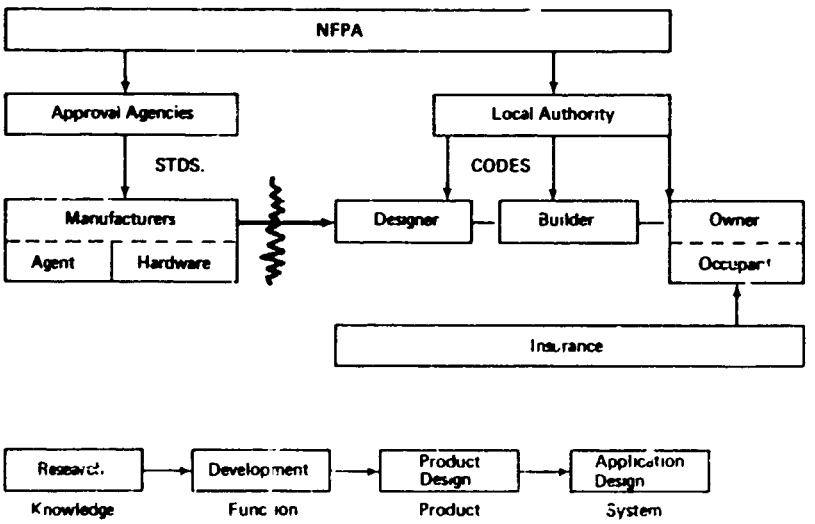

FIGURE 1

The second group are engineers whose function is to reduce the research output to practice. The effort consists of two phases: the development engineer who achieves a function and the design engineer who embodies that function in a product or component of a system that is producible and marketable.

The third group are the applications engineers who relate the product to the demands of a hazardous situation and who design a system using components from one or more manufacturers to make up a system to control a potential fire situation. Their responsibility is the effective utilization of those products or components. You might say fire insurance rates, which are based on historical data, are a measure of his performance.

The feedback loop of this system is through NFPA, the largest and probably the most effective of our code writing consensus groups and through the approval agencies. The latter have developed a set of standardized tests representative of Class A and Class B fire conditions that are used to measure comparative values of extinguishing agents or systems.

The evaluation of the efficacy of agents and systems by the participants in this huge consensus system is done by one of two means: how the new agent performs when measured by these standardized tests or how it compares with agents that have been in use and whose characteristics and experience record are already quantified or intuitively understood.

My background and experience comes from this middle area where the outputs of research are translated to the applications groups, and this analysis of agent effectiveness will be based on how a product engineer looks at prior test data to measure effectiveness of an agent.

First let's look at the hazards. They can be either burning in an oxygen-rich or oxygen-starved condition and it has an extreme effect on agent performance. In general, fire tests are conducted in oxygen-rich environments except for the peak flammability suppression points which are obtained at a stoichiometric condition. Peak flammability data defines "worst case" conditions for total flooding application.

The combustibles used in tests are representative of commonly encountered hazards -- wood for Class A; and flammable liquids, such as gasoline, for Class B. The flammable vapors from Class A materials are usually carbon-hydrogen-oxygen groups and from Class B are carbon-hydrogen groups. Both degrade to CO_2 or H_2O on complete combustion. There is a direct ratio that measures the ease of extinguishment of each. Flames from Class A materials are a little easier to extinguish because of the oxygen link.

Some people tend to classify combustibles as A or B on the basis of the extinguishing agents that are effective on them and others do it on the basis of the burning characteristics. Class C is an anomoly in that it is primarily an ignition source usually involved with Class A materials. Most Class A materials very early in their burning

history are in effect behaving as Class B materials in terms of the demands on fire extinguishing agents. If the burning vapors are extinguished, the fire goes out and stays out. However, cellulosic materials, which have carbon in them, have the added problem that the carbon can combine directly with oxygen from the air, a trait also exhibited by certain metals. The problem in extinguishing such materials is that if the flame is extinguished, the glowing carbon can act as a heat source to evolve additional flammable vapors and also be hot enough to ignite these vapors, although an external source of ignition could be party, as in electrical equipment, to reignition. Class B materials in general will stay out once the flame is knocked out. However, here too, external sources of ignition could cause reignition. Plastics and rubber goods, particularly the latter, tend to start burning as Class B materials but after sufficient heat has been absorbed by the plastic or rubber, they behave as Class A combustibles. They can continue to evolve and ignite flammable vapors even if their flame is extinguished, assuming that the extinguishing agent is transitory in the fire area.

There are additional complications to defining representative hazards that are related to configuration, such as if it is a flat or surface fire, three dimensional, deep-seated, etc.

We thus have for the hazards:

Flammable gases

Flammable liquids

Flammable solids.

To cope with fires there are two primary application means used. One is to apply agent directly at the site of the fire and build up a concentration of agent to such an extent that the fire is extinguished in a local manner. This can be done either by local fixed systems where the location of the potential combustible can be predetermined, and the other is by manual application by portable or semi-portable extinguishers. Measurement of effectiveness on these methods of application in general will relate to the size of the fire and the indicator of the effectiveness is usually some factor based on the quantity of agent required to extinguish.

The second application means is by total flooding where an entire volume or area must be covered without respect to the size of the fire hazard. These are fixed systems. Fire extinguishing effectiveness is thus not related to the size of the hazard but only to its nature and configuration. The quantity of agent is then prescribed based on the area to be covered or the volume to be flooded.

At this time there are no good, representative, reproducible, standard tests for Class "A" and plastics-rubber combustibles under total flooding conditions. Therefore, this paper will deal only with known, verified, representative performance data on Class "B" agents -- flammable gas and liquids.

Now if we go back to defining effectiveness, the commonly used methods are:

By weight of agent

By volume of agent

By gross weight of the extinguisher or system

By space occupied by the extinguisher or system

By cost of agent

By cost of the extinguisher system

By cost-effectiveness of the system, including the installed, maintained, and recharges cost over a period of time relative to the probability of actuation

By probability of success

By potential gain over potential threat (such as fire extinguishing ability versus threats posed by the agents such as corrosion, reactivity, toxicity, and contamination)

By risk management

The latter is the total hazard of an entity (structure, processes, contents, and people) counterbalanced by protective systems plus probable residual loss.

$$\text{Hazard} = \text{Protection} + \text{Risk}$$

The right hand side of the above equation includes the insurance and insurability factors, and both tangible and intangible losses. A fire protection engineer would normally plan the protective systems to enable risk management analysis. The active fire extinguishing systems are only a part of this total package of devices that prevent, retard, detect, and extinguish fire. A typical loss pattern would appear as in Figure 2 where measured loss, usually in dollars, is related to time of burning.

In general, if immediate action by people on-site can control or extinguish the fire, such as with a portable extinguisher, losses would be small. A second range of losses would result if the fire got beyond that capability or such systems weren't employed and the fire were contained or controlled by a primary fixed protective system, such as total flooding with a Halon agent or local application by automatic sprinklers. It is probable the Halon system would be closer to the left in terms of loss and the automatic sprinkler system closer to the right primarily due to the likelihood of faster detection and extinguishment with the Halon system. The third general loss area is when the primary system fails and the back-up system, such as municipal fire fighting department, must be brought in to complete the fire fighting. Risk management incorporates the

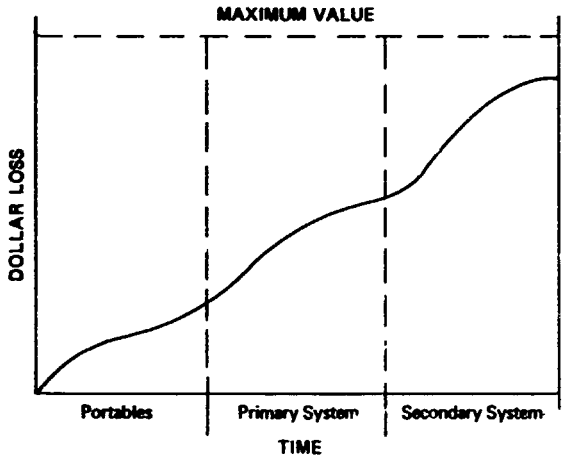

FIGURE 2

capabilities of each of these fire extinguishing systems and the probability of their effectiveness.

Now let's take a look at some actual performance comparisons of fire extinguishing agents.

There have been a great many supposedly definitive tests run on halons and other agents over the years. Some of the more notable Halon reports were put out by FRDL; Ansul-duPont; Purdue, Bureau of Mines; Dow Chemical Company, and the Naval Research Laboratory. The manner of conducting the tests, such as preburn times, fuels, configurations, and so forth can produce widely varying results. As an instance, local application tests of Halon 1211 and Halon 1301 from five different investigators over a ten year period showed that if Halon 1301 were assigned the value 100, Halon 1211 would vary somewhere between 55 and 198 in effectiveness relative to 1301.

When planning an extinguisher or extinguishing system for manufacturing and marketing, it is essential that it be measurable in the same terms that the applications engineer will measure it if any level of economics success is to ensue. A major stimulant to the development of extinguishing agents in this country took place in 1954 when Underwriters' Laboratories, Inc. adopted a system of measuring Class B capabilities of extinguishers on a series of test pans using controlled conditions for the fire environment and incorporating an operator of the portable extinguisher as part of the fire test rating. It has been in use for 18 years with little change and has provided application engineers with an invaluable reference for both comparative and absolute effectiveness.

An elegant tool that we use to identify the capability of extinguishing agents and to identify where certain extinguishers by size or configuration were not performing to "the-state-of-the-art" was to pool all published data on extinguisher ratings in the UL fire test systems, plot the data on log-log paper, and draw envelope curves at the peak points, using straight lines. A family of parallel curves develops for

each agent and enables one point to predict performance of an entire family of extinguishers. Fires up to 50 sq. ft. in area are conducted indoors and the extinguisher is required to have a discharge time of eight seconds or more. Larger fires are run outdoors and have a gradually increasing minimum discharge time requirement.

The time restriction imposed by UL and FM automatically narrows the ability of a manufacturer to exploit the rate of application characteristic on portable extinguishers. Figure 3 illustrates the general effect of rate and quantity on extinguishment.

Portables of necessity have to be the right hand side of the minimum quantity point. Fixed systems, particularly local application systems, can optimize agent performance by high flow rates. The minimum point is usually in the range of two to four seconds for most agents.

Figure 4, the envelope effectiveness curves of portable extinguishers, measures the relative Class B effectiveness on a unit weight basis. The chart can either be read horizontally to identify the amount of agent required to extinguish a specific fire size, or vertically to determine differences in effectiveness with the same amount of agent. Note that the quantity of agent is the amount in the extinguisher, not the amount actually used to extinguish the fire.

Marketing people would use the ordinate because the relative difference by percentage would be greater. That's called gamesmanship -- how to win without actually cheating. The more honest measure is to read horizontally and presume that extinguishers have been tailored to minimize the quantity of agent required to extinguish one particular fire size; that is, by holding the hazard constant.

Using this latter method, let's follow the product engineer's analysis of the data. In the halon family, I selected 1301 because a great deal of test work has been done on it by a number of authorities, there is a listed extinguisher of this type, and it is widely used in the Army. However, it is a gaseous agent on discharge and, as reported in many places in the literature, has certain limitations with respect to range. Therefore, a halon normally liquid at room

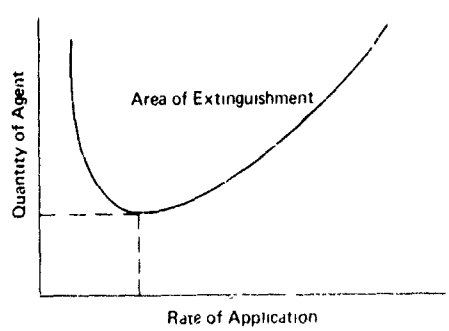

FIGURE 3

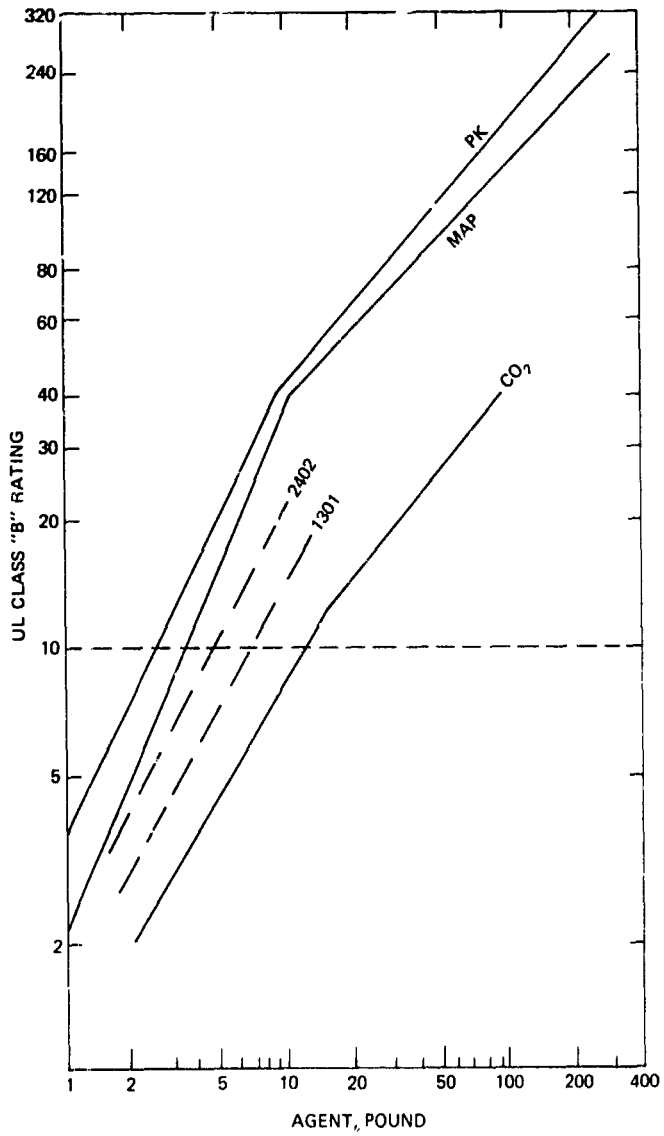

FIGURE 4

temperature was also used for comparison. The one selected was 2402 because it proved to be more effective on UL pan fire tests than either carbon tetrachloride, the only previously listed liquid extinguisher, or CB which is widely used in the Air Force. Carbon dioxide was used for comparison because it has a long history and it is a gaseous extinguishing agent that functions on a different and less effective mechanism of extinguishment than the Halons. Two dry powdered materials were used: monoammonium phosphate because it is repidly becoming a major fire extinguishant and is about as effective as sodium bicarbonate, and potassium bicarbonate because it is the most effective agent currently listed.

A factor in optimizing performance of extinguishers with these agents is that the gaseous and liquid agents can only utilize hardware improvements whereas the dry powdered materials are also capable of

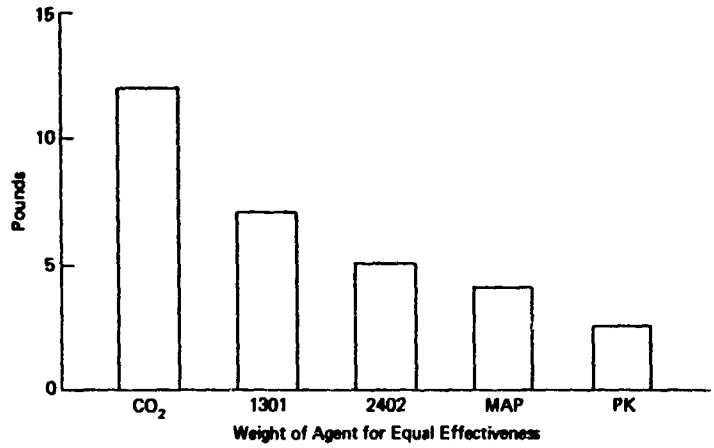

FIGURE 5

being altered in characteristic by control of particle size or surface area. The range problem imposed by the UL test method is judged by most using authorities to be a reasonably demanding characteristic of an extinguisher.

Figure 5 illustrates the relative effectiveness of these agents on a unit weight of agent basis for a UL 10-B rating (25 sq. ft. of heptane) with a one minute preburn on a steel pan with a 6" freeboard and tested indoors under controlled draft conditions.

Some of these agents require containers with higher working pressures because of their physical characteristics, have differing problems of expelling to achieve maximum effectiveness or cause container materials selection and cost to vary by corrosion resistance requirements. These factors affect both cost and weight of the total extinguisher. Figure 6 illustrates the gross weight of the extinguishers for equal effectiveness.

Figure 7 shows a comparison based on the cost of the agent for the quantity required to extinguish the 25 sq. ft. fire -- the selected level of effectiveness. Agent cost is often improperly evaluated on a

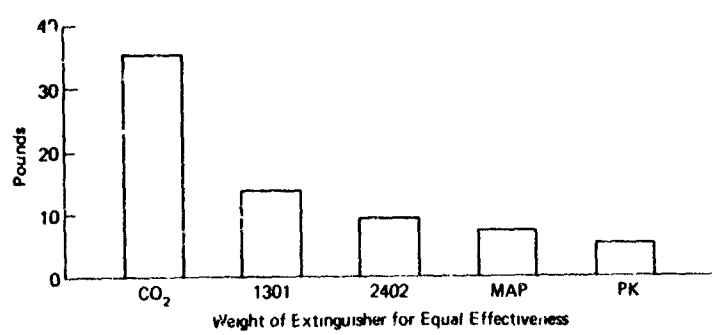

FIGURE 6

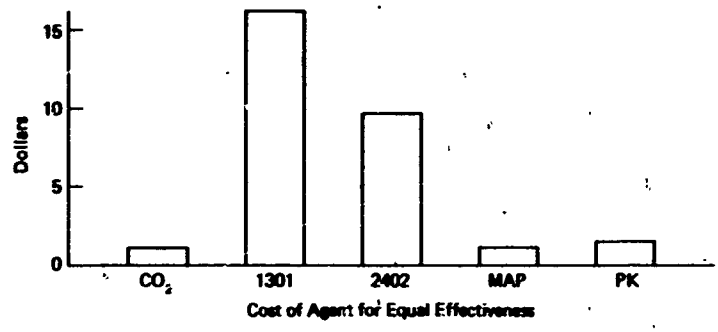

FIGURE 7

per pound basis and not on a per unit of effectiveness basis. This has had an adverse effect on acceptance of halons.

Figure 8 illustrates the cost of the complete extinguisher for equal Class "B" effectiveness.

Not only Halons have an agent cost stigma. Based on the number of extinguishers sold each year in this country, it must be concluded that the monoammonium phosphate and sodium bicarbonate extinguishers reach an acceptable performance level. Yet the superior Class B cost-effectiveness of potassium bicarbonate illustrated in Figure 8 is not prized except in extremely high hazard areas. The moderating influence in the purchasing pattern is probably due to comparing the cost of dry chemical agents on a unit weight basis without respect to Class B effectiveness, as shown in Figure 9.

No comparisons of the effectiveness of these agents on standard Class A fires are possible at this time since of this group of agents only monoammonium phosphate has achieved a Class A capability recognition on local application.

To structure comparative effectiveness of the Halons and other extinguishing agents in total flooding applications, the agent selection

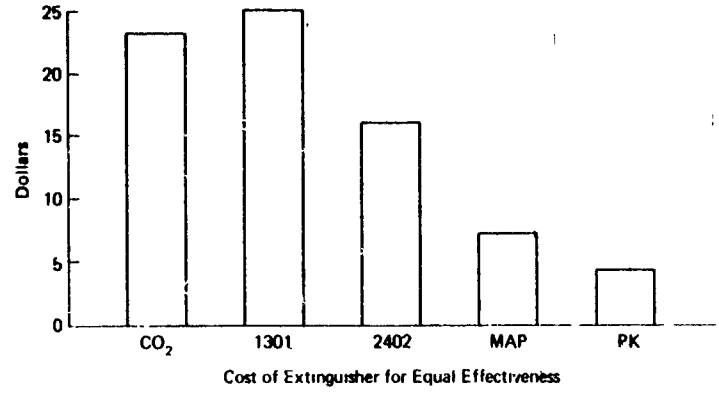

FIGURE 8

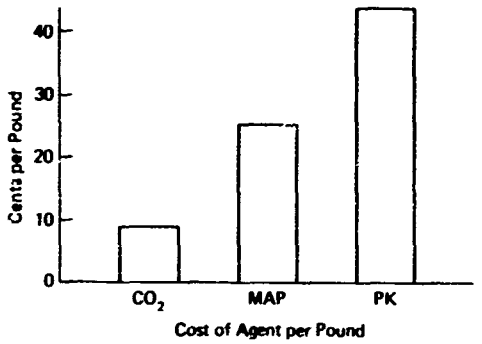

FIGURE 9

or the criteria for comparison are much more difficult. Extinguishment is achieved by indiscriminate distribution of the agent. This causes the scientist's bench-top tests of peak flammability to be applied directly in the marketplace. The quantity of agent required to extinguish on a unit volume basis has been reasonably defined over a period of years. The NFPA Standards 12, 12-A, and 12-B for CO_2, Halon 1301 and Halon 1211 respectively, furnish definitive data on a variety of common Class B combustibles for effectiveness comparisons.

The treatment of the data consisted of eliminating the safety factors on all combustibles common to these tables. The actual percent by volume to extinguish was then analyzed. A scatter graph revealed that there is a reasonable correlation between the quantity of the Halons versus the quantity of CO_2 required. Each of the combustibles was weighted on the basis of the quantity consumed in this country per year, assuming fire incidence relates to consumption. The difference between the flammable gases and flammable liquids was within ten percent so the data on each have been lumped in order to make a single effectiveness comparison.

It was not reasonable to include such agents as water from automatic sprinklers, high expansion foam or foam deluge systems in selecting the agents to use for the total flooding effectiveness comparisons. Sprinklers and foam are related to area rather than volume for their quantity demand for fire extinguishing and the others did not furnish a good basis for comparison. The cost of an entire system for fire control of a prescribed occupancy could present a means of evaluating the end-use effectiveness of all agents, but a risk management analysis would have to be used.

For convenience, only Halon's 1211 and 1301 were used from the Halon family. Halon effectiveness in total flooding is measured by peak flammability data so any of the reliable published reports can give comparable effectiveness indicators for other Halons. Specific combustibles will alter the agent demand used in these "averaged" data. The primary basis of comparison of these Halons is with carbon dioxide. There is a long history and familiarity with CO_2 by designers and owners of fire protection systems.

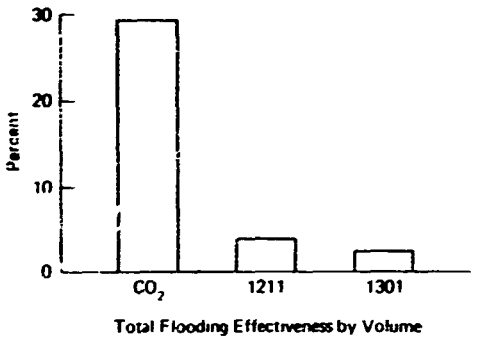

FIGURE 10

Figure 10 illustrates the relative effectiveness by volume. However, again we have a bit of gamesmanship because the agents are normally purchased by the pound and not by the cubic foot. The research laboratory methods lend themselves more readily to measuring volume, but the making and selling of systems using these agents is usually based on unit weight.

Figure 11 illustrates the relative effectiveness on a weight basis.

Figure 12 illustrates the cost of the agent for an equal unit of extinguishing effectiveness by total flooding. Figure 12 gives a false impression of excessive Halon cost if a systems engineering approach is not taken in the fire protection planning. When the cost of design, installation (including the container, piping and nozzles), agent, detection and actuators are lumped together, a totally different picture comes into focus as Figure 13 illustrates. Dampers and other means of agent confinement were not included in the systems cost comparison shown on Figure 13.

In conclusion, the Halons in portable extinguishers are about twice as effective as carbon dioxide on a unit weight basis and, in

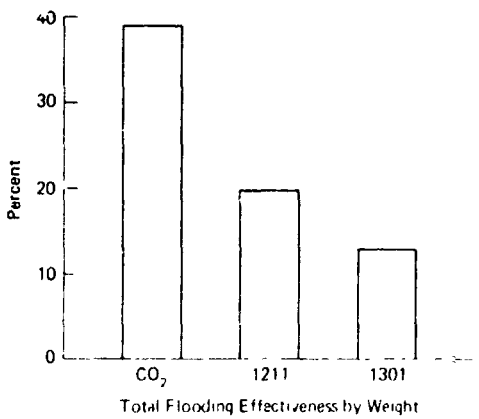

FIGURE 11

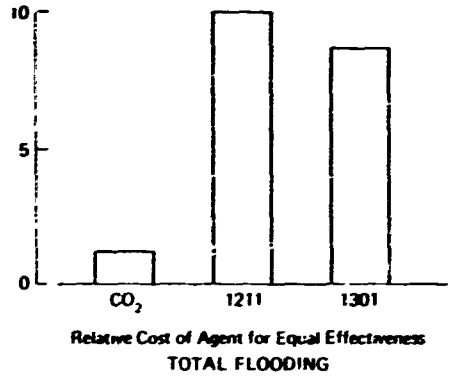

FIGURE 12

turn, are about two-thirds as effective as the dry chemicals. Within the Halon family, the liquid Halons are, in general, somewhat more effective than the gaseous extinguishing agents probably because of range. The prognosis for future utilization of Halons in portables would be in competition with carbon dioxide extinguishers where equal effectiveness can be achieved at the same or lower cost with much lighter weight, easier to handle extinguishers.

In total flooding, Halon 1211 is two times and Halon 1301 is three times as effective as CO_2 on a unit weight basis, and on a systems cost basis both are slightly less expensive than CO_2.

Recharge cost, when lumped with the total cost of a fire loss, is not significant. Local flooding, that is, building up an extinguishing concentration only where the combustible hazard is, could greatly enhance the cost-effectiveness of Halons.

Other attributes or requirements in any fire situation will influence the application engineer's selection of the agent or system. Later today and tomorrow you will hear discussion on specific hazards and the potential application opportunities for Halons. But, in the general institutional, commercial, industrial and transportation markets, these data are reasonably representative.

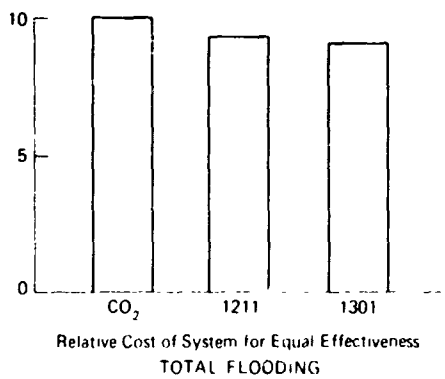

FIGURE 13

II TOXICOLOGY SESSION

Chairman, Herbert E. Stokinger

REMARKS

Dr. Christian: The second session this morning is entitled Toxicology, and will carry on through the afternoon. I would like to introduce to you the Session Chairman, Dr. Herbert E. Stokinger of the National Institute of Occupational Safety and Health.

Dr. Stokinger: I guess you have heard already the restrictions on time, and I will try to keep within the boundaries by making a very short introduction to the subject of principles and procedures for evaluating the safety of fire extinguishing agents.

Before beginning my profound presentation, I want to thank those presenters who were so considerate and kind to respond to the request to send in their manuscripts. In my harried world of the National Institute of Occupational Health and Safety under OSHA, which many corporate industrial hygienists, frustrated by the Act, have dubbed the Occupational Skepticism and Frustration Act, and in my job of trying to get this Act under way, where every other day is either a crisis deadline, or a deadline crisis, having those manuscripts ahead of time to pore over at night and on weekends went a long way to ease my task in handling this Toxicology Session, and particularly in coping with the general discussion that follows the end of the presentations this afternoon.

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PRINCIPLES AND PROCEDURES FOR TOXICOLOGIC AND PHYSIOLOGIC EVALUATION OF THE SAFETY OF MATERIALS

Herbert E. Stokinger

National Institute of Occupational Safety and Health

INTRODUCTION

The responsibility of manufacturers has historically been to evaluate the safety of their products under "ordinary conditions of use." For fire-extinguishing agents, ordinary conditions of use include not only the toxicology of the agent itself but that of all its pyrolysis products. So we have at the outset a dual problem: safety evaluation of the fire-extinguishing agent and its pyrolysis products.

In Table 1 are outlined the various procedures currently used for the evaluation for the safety of materials generally. Particularly noteworthy is the increasing emphasis given to using human volunteers as subjects.

THE FIRST PRINCIPLE

The principle on which the use of human volunteers is based is: the best study of man is man himself. The translation of results obtained on animals to man is always fraught with uncertainty, conjecture and doubt. As fire fighters are men and not laboratory animals, the use of human volunteers for developing toxicologic information is doubly warranted.

FURTHER REASONS FOR THE USE OF HUMAN VOLUNTEERS

There are two broad areas in toxicology where man is an essential test specie:

1. Those substances for which animals either respond differently than man, or not at all, and for which no industrial experience is available;

2. Those substances which produce:

   a. Predominantly sensory effects:

      (1) Irritants to the eye, skin, mucous membranes; e.g., SO_2, HCHO;

      (2) Headache, nausea, dizziness; e.g., CO;

TABLE 1. Procedures for Developing Industrial Air Standards (TLVs)

SHORT-TERM (ACUTE)

ANIMAL		MAN
Toxicity Range-Finding Tests		Single Inhalation Exposure
Single Dose LD_{50}, LC_{50}		Object: Sensory Effects
Oral	4-Hr. Inhalation	
Skin Absorption	Eye Irritation	Daily Repeated, 1 or 2 Weeks
Skin Irritation	Skin Sensitization	Extensive Tests for Signs and Symptoms of Toxicity and Behavioral Changes
		Object: Determine No-Effect Level

LONG-TERM (CHRONIC)

ANIMAL

Subchronic Inhalation, 30-90 Days, 2 or 3 Species

Object: Determine Level of 1. Toxicity Effects 2. Borderline 3. No Effect

Chronic Inhalation, 1-2 Yrs., 2 or 3 Species

Object: Determine No-Effect Level and Safety Factor

INDUSTRIAL EXPERIENCE

Environmental and Medical Surveys of Workers

b. Cutaneous sensitization; e.g., Dichloronitrobenzene;

c. Metal fume fever; e.g., Metal oxides.

ANIMAL STUDIES ESSENTIAL PRELIMINARIES

Before human volunteers are exposed, however, all new materials must have been thoroughly tested in animals. As Table 1 shows, this is accomplished first by so-called Range-Finding Tests. These are performed as single-dose experiments, usually on rats, to determine the LD_{50} by oral administration or the 4-hour LC_{50} by inhalation. Skin absorption and irritation and sensitization as well as eye irritation studies are performed in rabbits and guinea pigs to determine the toxicologic effects by all normal routes of entry.

PRIMARY OBJECTIVES

The primary objectives of the Range-Finding Tests are (1) to get a toxic-hazard evaluation by all normal routes of entry so that a precautionary label may be written; (2) to afford comparison with acute toxicities of other substances, such as are found in the Toxic Substances List of the National Institute for Occupational Safety and Health; (3) to form an idea of the nature of the toxicity and its limits, so that well chosen levels of exposure may be used in the subchronic and chronic long-term studies, because the next toxicologic procedure after the acute Range-Finding Tests have been made is, as is shown in Table 1, to determine the effects in subchronic and chronic studies.

The main objectives of these long-term studies as shown in Table 1 are: (1) to determine the character of the toxic effects; (2) the levels of exposure at which borderline effects occur and (3) the so-called "No Effect" level. From the latter two studies, an idea of the magnitude of the safety factor is obtained.

Omitted from Table 1 are tests for teratogenicity, a subchronic test procedure. Similarly, tests for carcinogenicity and mutagenicity are omitted from the chronic procedures because there is no reason to believe that such tests are necessary by virtue of the structure of the halocarbons and the principal modes of exposure. (We could be wrong!)

After these studies have been made, but not until exact knowledge of the type of toxicity has been determined, as well as what levels are safe, should human exposures be made.

THE SECOND PRINCIPLE -- TAILORING THE SAFETY EVALUATION TO STRUCTURE AND USE OF SUBSTANCES

What specific character the human studies will take depends upon a second principle, tailoring the safety evaluation to the nature and use of the test substance. In the case of the HALOCARBONS, used as fire-extinguishing agents, human exposures should mimic the exposure period of use. Exposure periods may be of three types:

1. Six- to seven-hour daily repeated industrial exposures.

2. Brief exposures occasionally repeated, as in fire-fighting.

3. Momentary exposure of rare occurrence, as derived from sprinkler systems.

4. For exposures to the pyrolysis products, above procedures 2 and 3 should be repeated for these substances.

An example of how experimental tailoring is applied under special environmental conditions to the toxicologic evaluation of halocarbons will be described by Douglas Call later in the Symposium when he will discuss the Hypobaric Toxicology of Halogenated Hydrocarbons. Another example where tailoring investigations have been made that are related to the particular structure of the halocarbons will be discussed by Back and Harris, who will describe the special cardiac effects of the halocarbons.

REMARKS

Dr. Stokinger: And now I will call upon Dr. Richard Stewart who will describe the procedures for evaluating the safety of materials in human subjects in what is unquestionably the most advanced laboratory of its kind. Dr. Stewart is a pioneer in this type of work and will show the shape of things to come in safety evaluations using human volunteers.

USE OF HUMAN VOLUNTEERS FOR THE TOXICOLOGICAL EVALUATION OF MATERIALS

Richard D. Stewart

Medical College of Wisconsin

Man is the ultimate toxicological test animal. While much can be learned from the laboratory animal regarding mammalian toxicology, only investigations with man can result in the acquisition of a reliable, comprehensive data base.

To date, only limited human exposures to known concentrations of Halon 1211, 1301, or 2402 have been conducted. Most of our information regarding the human toxicology of these three agents has been extrapolated from laboratory animal investigations. These data indicate that the limiting exposure safe for humans will be determined by the effect of these Halons on man's cardiovascular and central nervous systems. The determination of this no-effect exposure can be made only by studying a representative human population, because exposure to a Halon capable of producing an ataxic gait in a chimpanzee might be sufficient to produce profound central nervous system depression in man while an exposure judged to produce no effect in the mouse might possess the potential for inducing a cardiac arrhythmia in man.

There are three good sources for this "essential" human toxicological data. The first becomes available when a new compound is synthesized and laboratory personnel come into contact with it. If these personnel are, as they should always be, under careful medical surveillance, invaluable human data often can be acquired. The second source of human data is that obtained under carefully controlled conditions using human volunteers. It is the elaboration of this subject with which this communication is concerned. The third, and perhaps the best source of human toxicological data, is gleaned from properly designed prospective studies involving populations exposed to a chemical agent under a variety of normal use and abuse conditions.

Let us now focus our attention on the controlled-environment chamber and the use of human volunteers with which to acquire vital human toxicological data. Before any human experimentation can be commenced, there are both ethical and technical requirements which must be met. First, the governing philosophy for all human experimentation should be that set forth in the Declaration of Helsinki by the World Medical Association. Second, the research protocol should have had peer review by a human research committee whose members have been drawn from multiple scientific disciplines. Third, the human subjects must be true volunteers who are intellectually capable of comprehending and

FIGURE 1. 3200 cubic feet, Controlled-Environment Chamber, Medical College of Wisconsin, viewed through its observation window. All activities are filmed and stored on video tape.

evaluating the potential risks involved. The subjects should be required to sign an informed consent document which summarizes the purposes, the design, and the potential risks of the experiment. Fourth, prior to and following any experimentation, each subject's health status must be competently defined by a comprehensive medical examination with appropriate clinical laboratory studies. Fifth, all experiments should be performed under the direct medical surveillance of a competent physician, skillful in the handling of acute medical emergencies. Emergency medical equipment and supporting personnel must be immediately available.

Scenes detailing the acquisition of human data in the controlled-environment chamber of the Medical College of Wisconsin are shown in the sequence of photographs.

The controlled-environment chamber, viewed through the large observation window of the command laboratory in Figure 1, is a 20' x 20' x 8' room equipped with an independent ventilation system for the control of the contaminant, temperature, and relative humidity. The ventilation has been so designed that there is no concentration gradient of an airborne contaminant from wall to wall or from ceiling to floor. The chamber is equipped so that behavioral, intellectual, and physiological studies can be performed with sedentary or exercising subjects.

The Department of Environmental Medicine uses the team approach to conduct a human toxicology experiment. The current research team is

FIGURE 2. A team of experts representing several scientific disciplines is required to conduct controlled-environment chamber experiments with humans.

shown in the command laboratory immediately adjacent to the controlled-environment chamber (Figure 2). The team consists of two physicians, two environmental chamber engineers, a computer technician, a bioengineer, two staff members who administer the various tests within the chamber, and two analytical chemists. Not pictured are the consulting neuropharmacologist and the experimental psychologist.

The pure contaminant is contained in the walk-in hood to the left of the chamber beneath the two clocks in Figure 2. From there it is metered into the incoming air supply which enters the chamber through four diffusers in its ceiling. The concentration of the contaminant is continuously monitored by at least two independent analytical systems. For the majority of compounds under investigation, the chamber air is continuously monitored by an infrared spectrometer equipped with a long path length gas cell.

The second independent analytical system generally employed is a gas chromatograph equipped with an automatic sequential sampling valve connected by a sampling probe to the interior of the chamber (Figure 3). Usually, the same instrumentation that is used for monitoring the concentration of the chamber's contaminant is utilized for the detection of the contaminant in human breath, blood, and urine.

Signals from the chamber air monitoring equipment go directly to the PDP-12 computer (Figure 4) in addition to being recorded on a strip-chart. Each minute the chamber contaminant concentration is displayed

along with the cumulative chamber contaminant concentration. This provides a ready means for achieving fingertip control of the concentration of the contaminant under investigation. In addition, the computer is programmed to collect and promptly analyze the majority of the physiological data at the time of its acquisition.

On an hourly basis, during each exposure, a series of calibration standards are prepared in 15-liter saran bags and drawn through the air sampling system to the analytical equipment outside of the controlled-environment chamber (Figure 5). The computer is programmed to recognize these samples as calibration standards and automatically modifies the original calibration curves. At the conclusion of the experiment, all exposure data are recalculated based upon the final and most refined calibration curve.

Since the majority of the experiments are conducted in the double-blind mode, critical portions of each are filmed with closed-circuit TV for future review and appraisal.

Prior to each chamber exposure, a volunteer subject is given a repeat medical examination and biological samples are obtained for the appropriate pre-exposure baseline determination. In Figure 6 the subject

FIGURE 3. The analytical support laboratory for the controlled-environment chamber features a battery of gas chromatographs. Note the two chamber sampling probes extending down from the ceiling to the automatic sequential sampling valve. A video monitor of chamber activities rests on top of the refrigerator on the right.

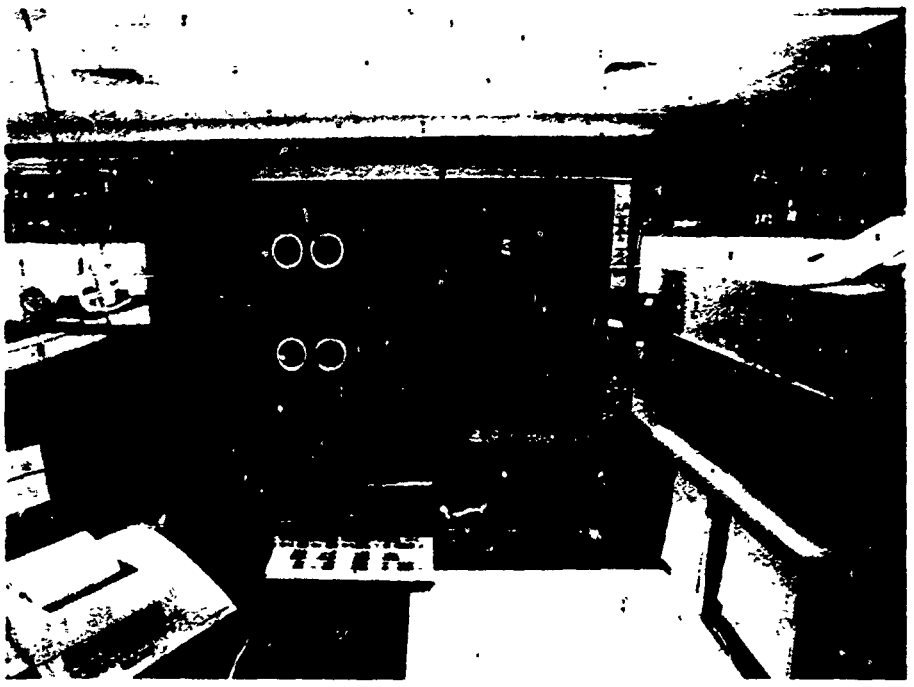


FIGURE 4. The "Nerve Center" for the controlled-environment chamber is the PDP-12 computer which provides data for the control of the concentration of the contaminant in the chamber as well as providing rapid analysis of physiological data.

is "wired" for EEG, EKG, visual evoked response recordings, and impedance cardiography with which to monitor the mechanical activity of the heart.

During the exposures, the subjective and physiological responses to the "environmental stress" are periodically monitored. In addition, tests are given to detect behavioral changes, alterations in physical performance, and to monitor organ function. One of the tests usually included in the test battery, the Flanagan Coordination Test, is being performed in Figure 7. It is sensitive enough to detect the alteration in manual dexterity induced by blood alcohol concentration of 50 mg %.

A recent addition to the cardiovascular monitoring equipment is the impedance cardiogram shown in Figure 6. By a rapid, non-invasive technique, the mechanical function of the heart may be monitored for 24 hours. Simultaneously, the electrical activity of the heart of each subject is telemetered to the monitors shown in Figure 8. In addition to providing visual monitoring and direct write-out rhythm strips, the electrical signals can be collected and analyzed by the computer.

The pressure within the controlled environment chamber is slightly lower than that in the adjacent command laboratory. Hence, it is possible to periodically obtain a blood sample from a subject by having him expose his arm through the blood-drawing port as shown in Figure 9. The pressure differential precludes contamination of the command

laboratory and permits the obtaining of a blood sample so that the blood concentration of the compound under investigation can be correlated with the results of the various test procedures utilized.

The exposure of human subjects in a controlled-environment chamber to precise concentrations of a compound for exact periods of time can yield valuable data regarding the absorption and excretion characteristics of the compound. An example of the precision with which absorption and excretion curves can be constructed is shown in Figure 10. Such data are extremely valuable for predictive and diagnostic purposes. With it, one can predict the approximate blood stream concentration of a compound and the resultant physiological effect for a projected exposure to a known concentration of the compound. Conversely, given the blood stream concentration of the compound in the post-exposure period, one can estimate the probable magnitude of the exposure and advance a reasonable prognosis.

In summary, the technology exists with which to safely acquire human toxicological data by exposing human volunteers to gases or volatile compounds in a controlled-environment chamber. In the chamber setting, most variables can be controlled, permitting accurate measurements of the physiological effects of the compound on man.

FIGURE 5. The important portions of each experiment recorded on video tape for future review. Here a subject is performing a modified Romberg test. To the left, one of the hourly calibration standards is being monitored.

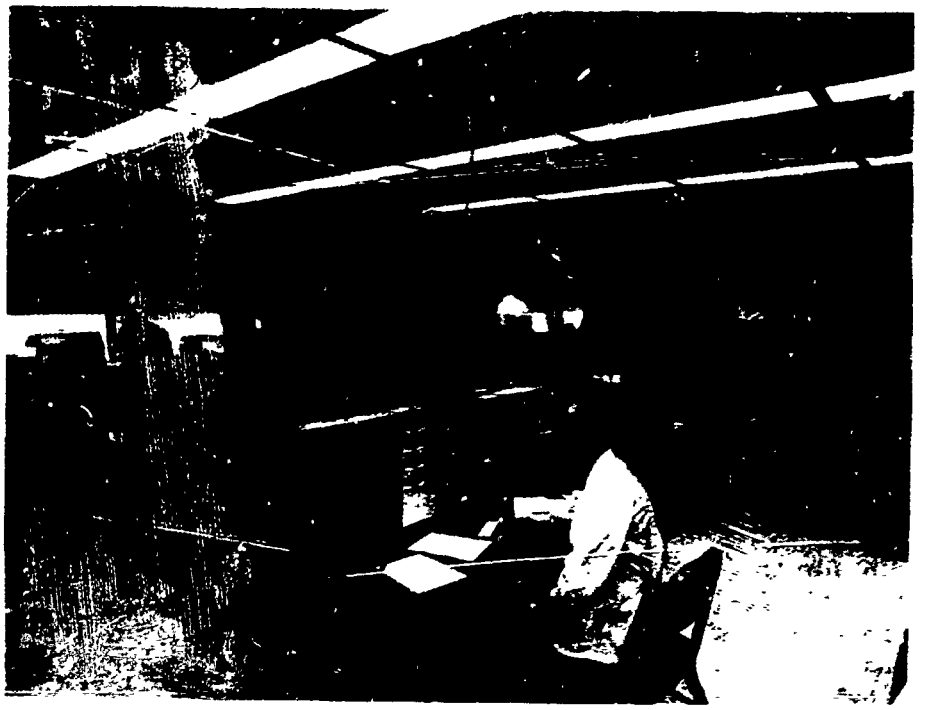


FIGURE 6. Experimental subject fitted with electrodes to monitor heart and brain function.

FIGURE 7. Subjects performing the Flanagan Coordination Test while being exposed.

FIGURE 8. The electrocardiogram is continuously telemetered from the exposed subject to the command laboratory.

FIGURE 9. The controlled-environment chamber is kept under slight negative pressure relative to the Command Laboratory which allows blood samples to be obtained in a non-contaminated area without interrupting the subject's exposure.

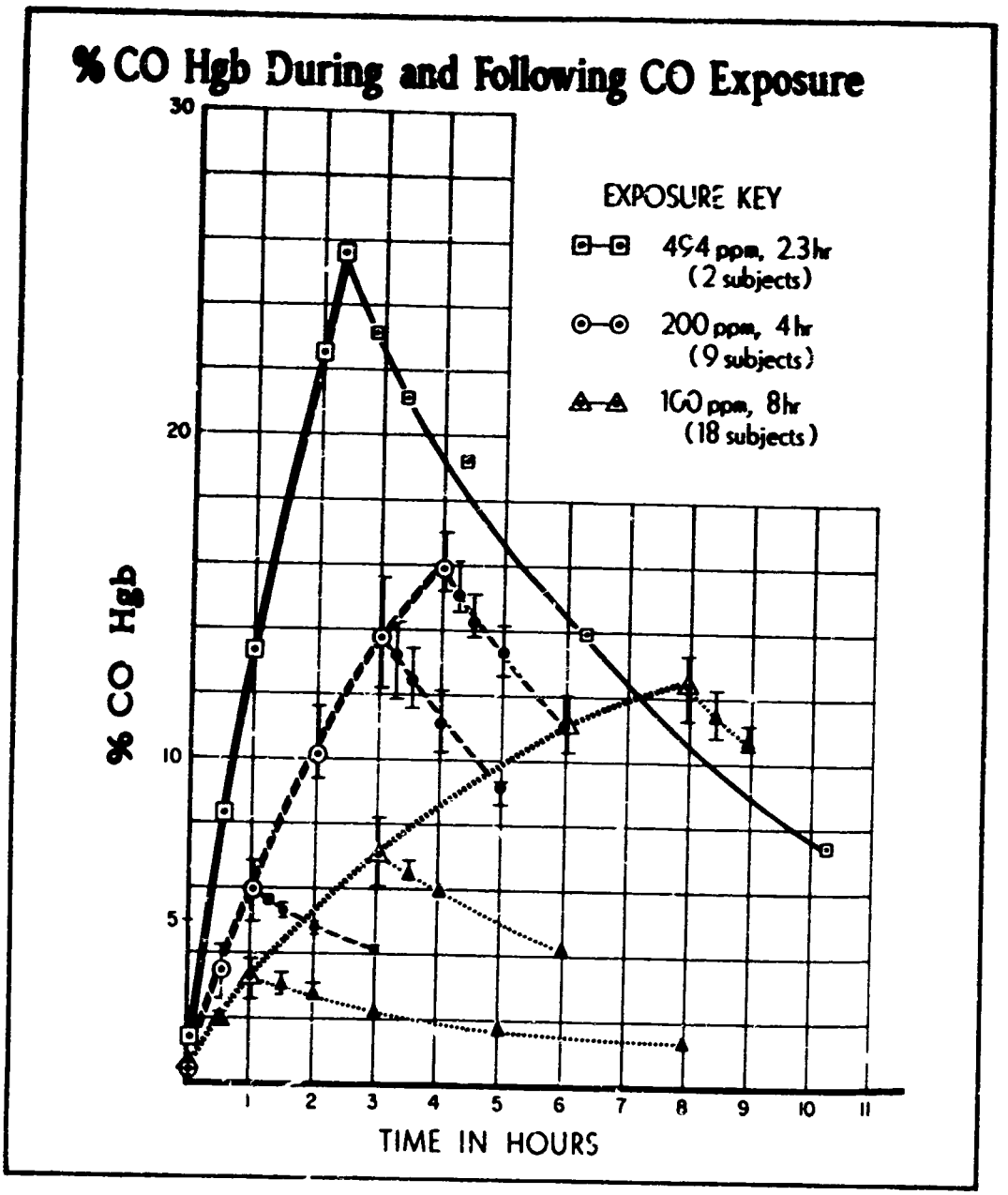


FIGURE 10. Carbon monoxide absorption and excretion in healthy, sedentary, non-smoking, white males. Reprinted with permission from the Archives of Environmental Health, Vol. 21, pp. 154-164, August, 1970.

DISCUSSION

Dr. Stokinger: I think you will all agree that there is a bit of sophisticated equipment there that registers a great deal of sensitive response and, as a result of work on this dichloromethane giving such

large amounts of carboxy hemoglobin, the Threshold Limit Committee is giving serious consideration to lowering the industrial air standard for this substance.

We are rather short of time, but may we take a minute for a question or two. Is there any question, comment or discussion of this presentation of Dr. Stewart?

Dr. Einhorn: In your studies I saw you had some results with carboxy hemoglobin. Have you monitored enzymes, cytochrome oxidase, acetylcholine and others?

Dr. Stewart: Yes, depending on the nature of the investigation. Since we have about five investigations, we have been looking at additive and synergistic effects when one gets a mixture of compounds, and usually in our laboratory setting it is a simple mixture, like a solvent plus a drug like phenobarbital, to see whether or not the presence of one or the other alters the metabolism of one or the other. So we have gotten into this in a rather simplified sort of fashion. But your implication is a very good one, that with man one needs to look at the very complex situation in which man normally moves, because exposure to a freon hair spray, for example, might dramatically, over a period of weeks, alter one's response to a commonly-used therapeutic agent.

Dr. Einhorn: May I just ask one more question? Are you looking at such factors as nerve impulse changes or muscle activation and contraction, in addition to response?

Dr. Stewart: Specifically no. We have looked at nerve conduction times and various evoked responses.

REMARKS

Dr. Stokinger: I think we will have to close the discussion because we are getting along here in time and running behind. The next speaker on the program is Dr. Zikria. Would you come to the podium and present your material on the effects of smoke inhalation from combustion materials.

INHALATION INJURIES IN FIRES

Bashir A. Zikria

Columbia University College of Physicians and Surgeons

Respiratory burns and smoke poisoning must have been known since the day Prometheus stole the fire from Vulcan and brought it to man. However, the scientific and medical meanings of inhalation burns and smoke poisoning are still not well understood.

In 1962, Phillips and Cope (1) labeled respiratory tract damage as "a principal killer" in burn victims. In 1967, Stone reported respiratory involvement in 15% of 197 burn patients studied (2).

In 1971, we analyzed the causes of death among fire fatalities which had occurred in New York City during the years 1966 and 1967 (Table 1). Three hundred and eleven of the 534 fire victims were autopsied, 60% of whom had died at the site of the fire or on the way to a hospital. Seventy percent of these early fatalities had respiratory involvement.

TABLE 1

Burn Mortality - New York City 1966 and 1967

	Total Cases 534 (Survival Time)		Autopsied Cases 311	
PBST	Cases	%	No. Cases	%
< 12 hrs	283	53	185	60
> 12 hrs	158	30	72	23
Not Known	93	17	54	17
Total	534	100	311	100

One hundred and five of the fire fatalities had less than 40% body surface burns; 77% of these could have been expected to survive, if statistical prediction were based solely on the extent of the body surface burns. Respiratory involvement was found as a primary diagnosis among

the majority of these fatalities. Specifically, 43% had smoke poisoning and/or asphyxiation; 50% had carbon monoxide poisoning; and 27% had pathologically evident damage to the tracheobronchial tree and lungs (Table 2). These figures clearly indicate the magnitude and seriousness of the problem of inhalation injuries in fire victims.

TABLE 2

Respiratory Complications with Body Surface Area Burn Less Than 40%

Cases	Aver. POS	Respiratory Comp.	
105	77%	80	(75%)

a.) Smoke Poisoning/Asphyxia 45 (43%)
b.) Carbon Monoxide Poisoning 53 (50%)
c.) Respiratory Pathology 28 (27%)

At present, it is generally accepted that the tracheobronchial tree and pulmonary tissues can sustain heat damage, chemical damage, anoxic damage, or any combination of these injuries in exposure to fire. Pressure damage may also occur when the fire is accompanied by an explosion.

HEAT DAMAGE

Until recently, many investigators doubted that caloric inhalation damage could occur in the tracheobronchial tree, because of the low specific heat of gases. Moritz's experiments on dogs in 1945, using high temperature torches as the source of combustion, seemed to indicate the physical impossibility of caloric damage (3). However, in 1968, both our group and other investigators (4,5,) demonstrated not only heat fixation of the tracheal mucosa in fire victims, but the presence of varying degrees of injury to the tracheobronchial tree. In our study, all the victims who had severe tracheobronchial damage were dead at the scene of the fire or soon after. Determinations of heat damage were subsequently made by early bronchoscopic examination in living patients and by gross and microscopic observations in those who were dead on arrival at hospitals (1). It is possible that the caloric burns of the tracheobronchial tree may occur by the inhalation of incompletely combusted products, which continue to burn on the way down the tracheobronchial tree. It is probable that Moritz did not find caloric damage because the torches used in his study accomplished complete combustion and thus did not simulate the conditions of structural fires. There is further evidence supporting the possibility of caloric damage to the tracheobronchial tree in that similar pathologic and physiologic changes can be produced in the tracheobronchial tree of dogs by standardized steam burns.

However, these findings do not explain the respiratory insufficiency, pulmonary edema and tracheobronchial mucosal damage seen in smoke inhalation patients who do not have extensive body surface burns (Table 3).

TABLE 3

Body Surface Area Burn and Probability of Survival (BSAB AND POS) in 257 Autopsied Cases

	PBST under 12 hrs.			PBST over 12 hrs.		
	Cases	BSAB	POS	Cases	BSAB	POS
With BSAB	111	60%	32%	61	44%	41%
Without BSAB	23	0%	100%	4	0%	100%
BSAB not known	51	-	-	7	-	-

PBST = Post-burn survival time

BSAB = Body surface area burn

POS = Probability of survival

SMOKE POISONING

Our cause-of-death analysis of 185 early burn fatalities (i.e., those surviving less than 12 hours) revealed that smoke poisoning was the primary diagnosis in 119 victims (Table 4). Also, the incidence of CO poisoning in those who had smoke poisoning was very high, 98 out of 124 fatalities (Table 5). Lethal levels of CO poisoning were discovered in 45 of the 185 early deaths (Table 6).

These findings are consistent with the data from our smoke experiments on dogs, in which the most common and immediate poisoning was carbon monoxide poisoning (6). In 1971, Kishitami of Japan (7) exposed mice to the smokes of cedar, wood-wool cement board, fire retardant plywood, melamine finishing board, polyvinyl chloride, polyurethane, polystyrene, phenol resin, and acrylic resin. From these studies he concluded that carbon monoxide must always be considered as the greatest potential danger to fire victims. However, our studies indicate that carbon monoxide alone cannot account for the pulmonary edema, tracheobronchial and pulmonary parenchymal damage resulting from smoke poisoning.

In one set of experiments, we exposed dogs to standardized smokes of wood and kerosene without heat in a smoke chamber (Figure 1). The animals exposed to kerosene smoke did not have any pulmonary edema, tracheobronchial or parenchymal damage, and all survived. On the other hand, the animals exposed to wood smoke did develop pulmonary edema and tracheobronchial and parenchymal damage, causing 50% of them to die within one to three days after exposure.

As a further test, soot particles from both wood and kerosene smoke were placed in the tracheobronchial tree of other animals (6). No damage and no mortality ensued. The soot from both sources was shown to be inert and therefore incapable of causing acute pulmonary damage. Carbon particles with water vapor which give visibility to ordinary smokes are basically harmless.

The carbon monoxide poisoning in dogs was overcome without sequelae, by artificial ventilation. When dogs were exposed to pure CO at the same levels present in the wood smoke, they did not develop pulmonary edema. Therefore, the pulmonary edema produced by wood smoke could not have been caused by CO, but must have been caused by other invisible constituents of the wood smoke.

Wood smoke and kerosene smoke were analyzed by mass spectrometry, gas chromatography and chemical analyses (Table 7). These studies showed that the concentration of aldehydes in wood smoke is 20 times that found in kerosene smoke. We know from previous work that the aldehydes are well-known irritants of mucus membranes (8,9). The most toxic of these aldehydes is acrolein, a three-carbon compound, for which the

TABLE 4

Respiratory Tract Complications in 257 Autopsied Cases

	PBST < 12 hrs (Survival Time)		PBST > 12 hrs (Survival Time)	
	Cases	%	Cases	%
Smoke Poisoning &/or Asphyxia only	99	53.5	4	5.6
Resp. Tract Damage &/or Pulmonary Damage Only	11	.9	28	38.9
Both	20	10.8	1	1.4
Neither	55	29.9	39	54.1
Total	185	100.0	72	100.0

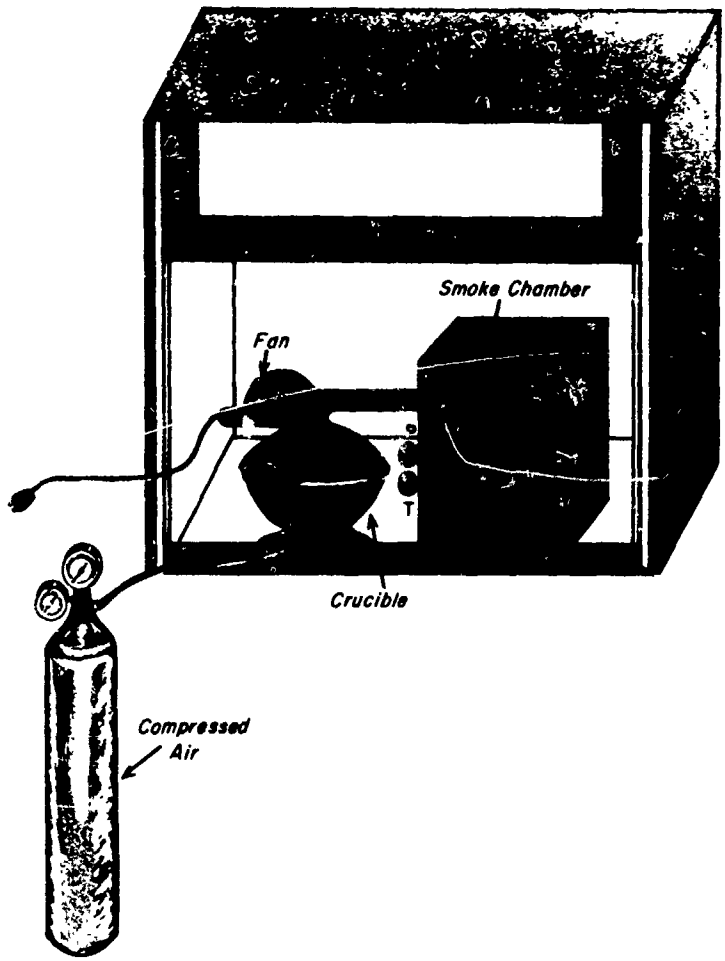


FIGURE 1. Smoke-producing crucible and the chamber with trap door were kept under a large exhaust hood.

maximum allowable concentration in industry is 0.1 ppm (Table 8). This particular aldehyde was present in the wood smoke analyzed in this study in a concentration 50 times that found in the kerosene smoke and 500 times the industrial maximum allowable concentration. In experimental animals, these aldehydes have caused pulmonary edema and death. Specifically, acrolein in a concentration of 5.5 ppm has been shown to cause irritation of the upper respiratory tract; at higher concentrations, pulmonary edema occurs; and at a concentration of 10 ppm, death occurs within a few minutes (9). In human male volunteers, inhalation of acrolein causes lacrimation and irritation of all exposed mucus membranes at concentrations of as little as 0.805 ppm (10). Short chain aldehydes which are major irritants were found in high concentrations in smoke from the combustion of household materials, such as furniture and cotton clothing (Tables 8,9).

Although these experiments identified carbon monoxide and aldehydes as the poisonous gases from wood and kerosene smoke, there is no doubt that other poisonous gases such as SO_2, SO_3, NO, NO_2, HCl, HCN, chlorine, fluorine, and possibly some others, can also cause respiratory damage when produced in significant concentrations from the combustion of other materials or vaporizing fumes.

SUMMARY

Inhalation injury probably is the most common cause of early death among fire victims. This injury, which involves the tracheobronchial tree and pulmonary parenchyma, is a direct contact injury. At present, it is believed that this injury is caused by two main components of the fire, i.e., (1) the actual flames or (2) the smoke and fumes, or their combination. The flames contain the products of incomplete combustion which may continue to release heat following inhalation, burning the mucosa of the tracheobronchial tree. In this case the injury is inflicted by heat denaturation of tissue proteins, causing cellular damage and death. When smoke and fumes from fires are inhaled, carbon monoxide poisoning commonly occurs along with the smoke poisoning. The toxicity of CO results from its binding with hemoglobin and replacing the oxygen, producing carboxyhemoglobin. CO poisoning, however, is reversible without sequelae, if resuscitative treatment includes good ventilation and high oxygen concentrations.

Another group of poisonous gases isolated from ordinary smokes, the aldehydes, also denature proteins, causing cellular damage and death. Poisoning by aldehydes may not be reversible. Experiments indicate that aldehydes bind irreversibly with the H bonds of amino acids and with RNA of respiratory tissue proteins.

Nitrous oxides, halogens, ammonia, hydrocyanic acid fumes and other poisonous gases which damage the respiratory tissues may also be present in smokes and fumes of fires, depending on the sources of combustion.

TABLE 5

Coincidence of Smoke Poisoning and/or Asphyxia with Carbon Monoxide Poisoning and with Respiratory Pathology

	Cases	Significant CO POISONING	Resp. Path.
Smoke Poisoning &/or Asphyxia	124	98 (77%)	21 (17%)

TABLE 6

Carbon Monoxide Poisoning in 185 Autopsied Cases, With Death Occurring Under 12 Hours

	Carboxyhemoglobin Saturation	Cases	%
Laboratory Determination		(130)	(70.3)
Usually Lethal	50%	45	24.3
Significant	11% - 49%	64	34.6
No Contribution	0% - 10%	21	11.4
Clinical Diagnosis Only		14	7.6
No Indication		41	22.1
	Total	185	100.0

TABLE 7

Smoke Analyses

CONSTITUENTS	KEROSENE VOL. %	WOOD VO. %
Mass Spectrometry		
Nitrogen	79.	76.
Oxygen	18.	16.7
Argon	0.94	0.95
Carbon Dioxide	1.03	2.85
Hydrogen	0.08	0.54
Benzene	0.18	0.17
Toluene	0.004	0.006
Methane	0.084	0.36
Gas Chromatography		
C_2 - C_6 Hydrocarbons	0.18	0.25
Carbon Monoxide	0.20	2.5
Chemical		
Total Aldehydes (Semiquant.)	0.007	0.11
Nitric Oxide	*ND < 0.0001	ND < 0.0001
Nitrogen Dioxide	ND < 0.001	ND < 0.0001

* ND = not detected below this level

Comparison of constituents of kerosene and wood smokes reveals significant quantitative difference in two poisonous gases, carbon monoxide and aldehydes.

TABLE 8

Smoke Analyses

Concentration p.p.m. Vol./Vol.

	WOOD	KEROSENE	COTTON	Industrial* M.A.C.
Acrolein	50	< 1	60	0.1
Formaldehyde	80	< 10	70	5
Acetaldehyde	200	60	120	200
Butyraldehyde	100	< 1	7	not tested

*Industrial maximum allowable concentration

The concentrations of four simple aldehydes in the smokes of wood, kerosene and cotton are shown against the maximum allowable concentrations in industry.

TABLE 9

Upholstery and Mattress Smoke

Constituents	Concentration % Vol./Vol.
Mass Spectrometer	
Nitrogen	76
Oxygen	17.0
Argon	0.90
Carbon Dioxide	1.55
Ethanol	3.7
Gas Chromatography	
Carbon Monoxide	0.16
Nitric Oxide and Nitrogen Dioxide	0.00011
Aldehydes	0.02(200 ppm)

REFERENCES:

1. A. Phillips and O. Cope, "Burn Therapy II: The Revelation of Respiratory Tract Damage as a Principal Killer of the Burned Patient," Ann. Surg. 155: 1, 1962.

2. H. H. Stone and J. D. Martin, "Pulmonary Injury Associated with Thermal Burns," Surg. Gynecol. Obstet. 129:1242, 1969.

3. A. R. Moritz, F. C. Henriques and R. Mc Lean, "The Effects of Inhaled Heat on the Air Passages and Lungs," Am. J. Path. 21: 311, 1945.

4. B. A. Zikria, W. Q. Sturner, N. K. Astarjian, C. L. Fox and J. M. Ferrer, "Respiratory Tract Damage in Burns: Pathophysiology and Therapy," Ann. N. Y. Acad. Sci. 150: 618, 1968.

5. H. H. Stone, D. W. Rhame, J. D. Corbitt, K. S. Given and J. D. Martin, "Respiratory Burns: A Correlation of Clinical and Laboratory Results," Ann. Surg. 165: 157, 1967.

6. B. A. Zikria, J. M. Ferrer, and H. F. Floch, "The Chemical Factors Contributing to Pulmonary Damage in 'Smoke Poisoning'," in Press, Surgery, 1972.

7. K. Kishitami, "Study on Injurious Properties of Combustion Products of Building Materials at Initial Stage of Fire," J. Facul. Engin. Univ. Tokyo 31: 1, 1971.

8. N. I. Sax, "Dangerous Properties of Industrial Materials," New York, Von Nostrand Reinhold, Co., 1968.

9. W. B. Deichmann and H. W. Gerarde, "Symptomatology and Therapy of Toxicological Emergencies," New York, Academic Press, 1964.

10. M. V. Sim and R. E. Pattle, "Effect of Possible Smog Irritants on Human Subjects," JAMA 165: 1908, 1957.

DISCUSSION

Dr. Stokinger: I noticed that one of your concepts of the structural rearrangement of sulfur dioxide with protein constituent of the lung leads to a CNS ring, thiazalidone, a component of saccharine, and which is under investigation as a carcinogen. We must be careful, mustn't we?

I think we have a minute or two for any comment or questions. This is a very interesting paper. I will discuss it a little later on.

Mr. Wands: Have you conducted any experiments where the animals were exposed to wood smoke after the wood smoke had been passed through a particulate filter?

Dr. Zikria: No, we did not. The only experiment where we used soot material, particulate material, we got it from the wood, collected it and standardized it at so many milligrams. Then we put it into the lungs through a bronchoscope in these animals. The animals coughed up the soot in a matter of 48 hours through 72 hours without any pathological findings following 21 days of observation.

Dr. Harris (University of Illinois Hospital): Perhaps the commonest cause of pulmonary edema is actually heart failure. I wonder if you have any evidence as to whether or not these aldehydes and other constituents might be causing rather rapid onset of left ventricular failure, which would contribute to pulmonary edema?

Dr. Zikria: I am sorry I did not bring another slide on the clinical state of carbon monoxide poisoning, or smoke poisoning. I do believe that whenever we do have those at levels of 5, 30 and 50 in patients, presumably there are these other toxins together with carbon monoxide. Although we were able to clear the carbon monoxide from their blood by good ventilation and high oxygen tension, they did continue to develop pulmonary edema, not truly on the basis of cardiac failure, although in some five patients that I have carefully studied, one of them was an elderly woman in whom that question could have arisen, but the others were firemen, very healthy young people, who did not seem to have any cardiac source of the edema. It appeared to be mostly an excitative reactive edema of the lung.

Dr. Harris: I can well believe that the latter certainly is true, but what I intended to suggest was the possibility that some of these organic compounds might be absorbed into the bloodstream, and depress myocardial contractility in a manner perhaps not shown, and that would lead to acute heart failure that might itself, or together with direct action of the smoke ingredients upon the lungs, lead to the pulmonary edema.

REMARKS

Dr. Stokinger: That is a good point. I think now I will have to call on Doug MacEwen to keep us on time here. He is going to talk on paper No. 4, "Toxicology of Pyrolysis Products of Halogenated Agents."

TOXICOLOGY OF PYROLYSIS PRODUCTS OF HALOGENATED AGENTS

James D. MacEwen

SysteMed Corporation

The toxicity of a candidate fire extinguishant and its pyrolysis products are matters of considerable importance in the selection of suitable fire-fighting agents. This is particularly true of the halogenated agents which are chemically changed in the process of putting out a fire. Although adequate information is available for comparison of the acute inhalation toxicity of most halogenated fire extinguishants to rodents, the available data on the toxicity of pyrolysis products are meager and difficult to compare. They are difficult to compare because uniform methods have not been used in obtaining the data and also because variations in temperature, fuel burned and available oxygen result in large differences in the amount of halogenated agent pyrolyzed and the chemical species formed.

Since the amount of thermal decomposition of the halogenated agents varies with temperature the more useful toxicity comparison studies have been conducted at 800°C at which point a contact time of two seconds should result in 100% pyrolysis. Comstock et al. (1953) reported the approximate lethal concentration for 15-minute exposures to rats on five Freons(R) as shown by decreasing order of toxicity in Table 1. The tests were conducted on single rats at each exposure level without measurement of completeness of thermal degradation and must therefore be considered as rough approximations. They do, however, show that Freon 1301 was much less toxic than the other materials tested.

TABLE 1

Approximate Lethal Concentration

15-Minute Exposures

Comstock et al. (1957)

Agent	Formula	ALC (ppm)
Freon 2402	$C_2Br_2F_4$	1,600
Freon 1202	CBr_2F_2	1,850
Freon 1011	CH_2BrCl	4,000
Freon 1211	$CBrClF_2$	7,650
Freon 1301	$CBrF_3$	14,000

Treon (1957) exposed cats, rabbits, mice and rats to nominal 20,000 ppm concentrations of Freon 1301 for varying times and four different temperatures. He found 100% survived after 18 minutes exposure at 700°C and 80-100% deaths for the same time period at 1090°C. These experiments resulted in 5% pyrolysis at the lower temperature and approximately 60% pyrolysis at 1090°C.

Studies conducted by the Toxic Hazards Research Unit of SysteMed Corporation in which rats were exposed to the pyrolysis products of $CBrF_3$ and CH_2BrCl yielded more precise LC_{50} data. In these studies the fire extinguishants were pyrolyzed in a hydrogen oxygen flame. Using the atomizer burner assembly of a hydrocarbon analyzer the materials were pyrolyzed at 800°C measured by a Chromel-Alumel thermocouple. The temperature was controlled by adjusting the fuel ratio. This technique of burning the Freon compounds in air differed from previous studies that passed the test materials through heated metal columns which may have resulted in some loss of the halogen acid gases formed.

The pyrolysis products formed during combustion of CH_2BrCl are shown in Table 2.

TABLE 2

Pyrolysis Products Formed During Combustion of CH_2BrCl at 800°C (ppm)

Measured Preignition Concentration	Equivalent Pyrolyzed Concentration	Strong Acid	HCl	HBr	Br_2
550	190				11
750	260				18
1000	350	270			
1000	350	230			
1575	675		350	36	
2000	725	470	380	23	
3000	1025				45
Average mole % of compounds formed		69±8	52±4	4.3±1.0	5.6±1.3

$COCl_2$ and Cl_2 not detected

The complete pyrolysis of this compound to HBr and HCl would have yielded 200 moles % of strong acid and 100 mole % of each individual acid. The actual combustion process resulted in approximately 30-50% pyrolysis and yielded 52 moles % of HCl with some HBr and Br_2 as seen.

A number of new organic compounds were found in the pyrolyzate (Table 3) which included two materials with enriched bromine content.

TABLE 3

Relative Concentrations (%) of Carbon-Halogen Compounds in Untreated Bromochloromethane and in Pyrolyzate

Compound	Commercial Material	Pyrolyzed Material
CH_2BrCl	98.60	96.20
CH_2Cl_2	1.00	0.74
CH_3NO_2	0.21	0.15
CH_2Br_2	0.19	1.44
CH_3Cl		0.02
CCl_4		0.01
$CHBr_2Cl$		1.27
CCl_3Br		0.18

The ignition of bromotrifluoromethane at 800°C produced three major inorganic products - HF, HBr and Br_2 as shown in Table 4.

TABLE 4

Concentration of Pyrolysis Products Produced by Ignition of Bromotrifluoromethane at 800°C

Measured Preignition Concentration	Equivalent Pyrolyzed Concentration	HF	HBr	Br_2
3920	2340	2280		283[a] 227[b]
3800	2070	2370	160	236[b]
Average mole % of compounds formed		106	7.7	11.3

[a]Spectrophotometric method.
[b]Volumetric method.

The pyrolysis of $CBrF_3$ at this temperature was approximately 48-58% complete as measured by difference between preignition concentration and unchanged $CBrF_3$ in the animal chambers.

The inhalation of the pyrolysis products of $CBrF_3$ generally produced delayed deaths in affected animals (Table 5).

TABLE 5

Results of Exposure to the Pyrolysis Products of $CBrF_3$
Military Specification MIL-B-12218-A

Measured Preignition Concentration (ppm)	Equivalent Pyrolyzed Concentration (ppm)	Pyrolysis (%)	Mortality Ratio	Day of Death Postexposure													
				1	2	3	4	5	6	7	8	9	10	11	12	13	14
3400	1700	50.0	0/10														
4000	1950	48.7	5/10				3	2									
4000	2100	52.5	5/10				4	1									
4000	2300	57.5	5/10	1		1	3										
5300	2750	52.0	6/10	1			2	3									
5950	3075	51.8	6/10	1	1		1	1		1				1			
6050	3250	53.8	8/10	2		1	2	1									2
7150	3780	52.9	9/10	5	3		1										
7900	4475	56.5	9/10	1	1	5	2										

These deaths characteristically resulted from pulmonary hemorrhage and edema which was more profound in animals that died during exposure or within 24 hours. Slight residual changes such as mild pulmonary congestion and emphysema were seen two weeks postexposure in animals surviving acute $CBrF_3$ pyrolyzate exposures at or near the LC_{50} level. The 15-minute LC_{50} value for pyrolyzed $CBrF_3$ calculated from these experiments was 2300 ppm for rats. This concentration of pyrolyzed $CBrF_3$ produced an HF concentration of 2480 ppm which is comparable to the 15-minute LC_{50} for HF of 2689 ppm reported for rats by Carson et al. (1961). Not only is the HF concentration produced at the $CBrF_3$ LC_{50} value comparable to the LC_{50} value for HF but the pathologic response and delayed death patterns are also similar, which leads to the conclusion that this compound is responsible for the observed toxicity.

Bromochloromethane pyrolysis products were found to be considerably more toxic with a 15-minute LC_{50} value of 465 ppm (CH_2BrCl equivalent). The pathologic response was rapid as shown in Table 6 with

massive pulmonary edema and congestion being observed in all lobes of the lung. Deaths usually occurred within eight hours postexposure and more were seen after the second day. The edema process was resolved in surviving animals and no significant pulmonary tissue changes could be found 14 days later. Although HCl was a major component of the pyrolyzate of CH_2BrCl the observed mortality could not be attributed to this compound and may be due to synergistic effects of the mixture of compound formed during pyrolysis.

TABLE 6

Results of Exposure to the Pyrolysis Products of CH_2BrCl

Measured Preignition Concentration (ppm)	Equivalent Pyrolyzed Concentration (ppm)	Pyrolysis %	Mortality Ratio	Day of Death Postexposure 0	1	2
550	190	34.5	0/20			
1075	355	33.0	4/20	3	1	
1050	360	34.3	10/20	10		
1050	450	42.9	9/20		9	
1050	460	43.8	15/20	13		2
1000	500	50.0	7/20	6	1	
1575	675	42.8	17/20	17		
1650	800	48.5	16/20	16		
2100	900	43.0	19/20	19		
3050	1025	33.5	19/20	18		1
3212	1413	44.0	20/20	20		

Another significant product formed during any fire, particularly in confined areas, is carbon monoxide (CO). Carbon monoxide combines with the hemoglobin of blood to form carboxyhemoglobin which interferes with the transport of oxygen to body tissues. Investigations were conducted to determine if the toxicity of the HF formed by prolysis of $CBrF_3$ was enhanced by the presence of carbon monoxide. These studies were conducted on rats and mice exposed to HF singly and in combination with CO for 5-minute periods. The atmospheric concentrations of HF were varied while a concentration of CO which produced 25% carboxyhemoglobin was held constant. There was a change in the slope of the mortality curve but carbon monoxide had no significant effect on hydrogen fluoride toxicity.

Freon 1301 ($CBrF_3$) appears to have the least toxic pyrolysis products of the halogenated fire-fighting agents tested thus far. The amount of this agent required to quench a fire may, however, result in sufficient production of pyrolysis products to produce toxic responses ranging from skin irritation to pulmonary edema. Consequently,

respiratory protection should be used for fire fighting with any of the halogenated agents.

REFERENCES:

1. T. R. Carson et al., "The Response of Animals Inhaling Hydrogen Fluoride for Single, Short Exposures," Aeronautical Systems Division TR-61-744, 284030, Wright-Patterson Air Force Base, Ohio, December, 1961.

2. C. C. Comstock and F. W. Oberst, "Comparative Inhalation Toxicities of Four Halogenated Hydrocarbons to Rats and Mice in the Presence of Gasoline Fires," Arch. Ind. Hyg. and Occup. Med., 7: 157, 1953.

3. J. F. Treon et al., "The Toxicity of a Purified Batch of Monobromotrifluoromethane (Freon 13 B-1) and That of Its Products of Its Partial Thermal Decomposition When Breathed by Experimental Animals," Kettering Laboratory Report, University of Cincinnati, Ohio, June 19, 1957.

DISCUSSION

Dr. Walter: I wondered what the relationship of your pyrolysis products to the pyrolysis products of this product actually used to extinguish a fire in a confined space is. It seems to me, as I recall these, these are manyfold higher than you find in a fire.

Dr. MacEwen: Could I have that question again, please?

Dr. Walter: The pertinent question I wanted to ask was the relationship between the pyrolysis products and their toxicity shown by this speaker, and their relevancy to the pyrolysis products actually discovered in a wild or native fire situation where as I have seen the data, the pyrolysis products are very small as compared to these exaggerated ones shown on the screen. I wondered if there was any data to show the relationship between them.

Dr. MacEwen: The purpose of these was not to prove that they would kill you in a fire, but to develop comparative data to show which would produce the more violent effect. It is quite possible that many fires in a test cell can be extinguished with the production of less of these irritating agents, hydrogen fluoride, hydrogen chloride, and so forth. However, the amount of these produced is dependent upon the total extent of a fire, and not necessarily that which you would find in a little test cell. In an aircraft fire, for example, you have quite a profound fire before you put it out.

Mr. Wilson: I think maybe a little light could be shed on this if I could take a liberty with your experiment and characterize it as taking a kettle full of water, putting it on the stove, getting steam, and saying I have got this much steam, and steam can be very dangerous if handled improperly. Applying water to a fire, many people for many years have said sprinklers, for instance, will create steam, and this steam will burn you, scald you. This is not true in practice, and I wonder if perhaps the value of your paper is not to say should we cook all of the agents, this is what we will get. When we actually attack a fire in a space with these agents, we do not produce anything like the amounts that you have been talking about.

Dr. MacEwen: I did not mean to imply that we were going to kill everybody with the use of these things. I did indicate, however, that much lower concentrations of these are extremely irritating to the mucus membrane, and, as I said, may go anywhere, depending on the amount, the amount of the fire, the amount used and the amount pyrolyzed may result in anything from mild irritation, some damage to the eyes and mucus membranes, to pulmonary congestion and pulmonary edema.

REMARKS

Dr. Christian: The session this afternoon will be a continuation of the Toxicology Session which was begun this morning. The session will be chaired by Mr. Ralph Wands who has graciously consented to take over for Dr. Stokinger so that he might sit in the audience and better take in the papers which are being given this afternoon. I am sure Mr. Wands is known to most of you. He is the Executive Secretary of the Committee on Toxicology.

Mr. Wands: Our first speaker comes to us from some distance and from a great deal of background and experience in the field of toxicology of the halogenated hydrocarbons, and particularly Halon 1211. Dr. David Clark from the Imperial Chemical Industries, England.

TOXICITY OF HALON 1211

David G. Clark

Imperial Chemical Industries Ltd, England

Since the original toxicological studies on halogenated fire extinguishants in 1950 (1), several papers have been published on the toxicity of Halon 1211 (bromochlorodifluoromethane) in experimental animals (2, 3, 4, 5). This present report describes briefly the toxicological and pharmacological actions of Halon 1211 in animals and man.

As normal exposure to this fire-fighting chemical is likely to be short, infrequent inhalation, the report is principally concerned with the acute effects of the inhalation of Halon 1211 itself. The effects of any possible thermal decomposition products are not discussed.

ANIMAL STUDIES

Rats and guinea pigs have been exposed to various concentrations of Halon 1211 in small atmosphere chambers and the concentrations causing death of some of the animals noted. Table 1 summarizes the results obtained by various authors. Animals exposed to these concentrations showed signs of a profound depression of the central nervous system before death, but those that did not die recovered promptly when exposed to fresh air.

TABLE 1

Concentrations of Halon 1211 Causing Deaths

Species	Lethal Concentration (vols %)	Time of Exposure (mins)	Reference
Rat	23	30	2
	32	15	1
	30	15	5
	22*	140	4
Guinea Pig	23	15 - 30	2

* Concentration increased with time.

The Underwriters' Laboratories conducted experiments in 1955 in order to classify the life hazards of various fire extinguishants (3). Guinea pigs were exposed to concentrations of the extinguishants from 0.5% to 20% for periods of time ranging from five minutes to two hours. Their classification is presented in Table 2.

TABLE 2

Underwriters' Laboratories Classification of Comparative Life Hazards of Various Fire Extinguishing Agents

Group	Definition	Example
3	Gases or vapors which in concentrations of the order of 2 to 2.5% for durations of exposure of the order of 1 hour are lethal or produce serious injury	Chlorobromomethane Carbon Tetrachloride
4	Gases or vapors which in concentrations of the order of 2 to 2.5% for durations of exposure of the order of 2 hours are lethal or produce serious injury	Dibromodifluoromethane
5a	Gases or vapors much less toxic than Group 4, but more toxic than Group 6	Halon 1211 Carbon Dioxide
6	Gases or vapors which in concentrations up to at least 20% by volume for durations of exposure of the order of 2 hours do not appear to produce injury	Halon 1301

More detailed studies have been conducted since these experiments were reported. Several species of animals have been exposed to Halon 1211 and the appearance and disappearance of the various toxic signs noted in an attempt to gain some insight into the mode of action of the agent, and to assess its possible hazards in a fire-fighting situation (4, 5).

Exposure of rats, mice, guinea pigs, rabbits, cats, dogs and a monkey to concentrations of Halon 1211 greater than about 10%, usually gave rise to slight tremors within 10 minutes. If these exposures were continued, or if higher concentrations were used, tremors, head shaking, ataxia and convulsions eventually occurred. On cessation of exposure

the animals recovered promptly without ill effects, but if exposures were continued, the animals eventually became comatose, failed to respond to stimuli, and their breathing became slower and more shallow until they died.

Although it is unlikely that prolonged daily exposures to Halon 1211 could occur in normal use, rats have been exposed to 1% Halon 1211 for six hours per day for three weeks. Slight lethargy only was noted; there were no biochemical or hematological changes noted and all the tissues were normal when examined histopathologically at the end of the experimental period (5).

Halon 1211, and the other halogenated fire extinguishants, are related to various chemicals that are known to make the heart hypersensitive to the arrhythmogenic effects of adrenaline (6). These arrhythmias can be minor changes such as ventricular ectopic beats, or major changes such as ventricular tachycardia or ventricular fibrillation, which can be fatal. Since high blood levels of adrenaline could be expected from the stress and fear of a fire-fighting situation, the cardiac sensitizing potential of Halon 1211 has been assessed (5).

Rats, rabbits and dogs were exposed to various concentrations of Halon 1211, usually for five minutes, and the cardiac effects of a large intravenous injection of adrenaline recorded. Only one rabbit showed evidence of cardiac sensitization when challenged with adrenaline during exposure to the maximum concentration of Halon 1211 that could be tolerated (4%). The hearts of anesthetized rats were more resistant than rabbits, since no cardiac arrhythmias could be produced even at a 10% level of exposure. Dogs, however, were particularly susceptible, and cardiac arrhythmias could be produced by the injection of adrenaline during inhalation of 1 to 2% Halon 1211.

An injection of adrenaline 10 minutes after exposure to a sensitizing concentration of Halon 1211, however, never resulted in arrhythmias (5). This observation, together with previous observations that Halon 1211 and related fluorocarbons are rapidly eliminated from the blood stream after exposure (5, 7) would indicate that cardiac sensitization is not due to permanent structural damage of the heart, but is a transient phenomenon, due to some temporary interaction of the Halon with adrenaline.

It is not possible to apply the results of the cardiac sensitization experiments directly to man because the dose of adrenaline injected may have been excessive and unphysiological (5, 8). Experiments such as these show merely that Halon 1211, like many other related chemicals (6, 7, 8, 9) has the potential to cause cardiac sensitization. Further experiments have therefore been undertaken in which dogs were exposed to Halon 1211 under stress conditions to see if the adrenaline released into the blood stream under these more physiological conditions was sufficient to cause cardiac irregularities (5). No abnormal heart beats were produced during a 15-20 minute exposure to 7% Halon 1211 despite the presence of severe convulsions, but one dog suddenly developed ventricular fibrillation during the convulsions induced by a 27-minute exposure to a 5% concentration.

HUMAN STUDIES

The animal experiments show that the principle toxicological effects of Halon 1211 are on the central nervous system and the heart. Halon 1211 can first stimulate, then depress the central nervous system to give muscular tremors and then anesthesia. It can also sensitize the heart to the arrhythmogenic effects of adrenaline. Since there is some variation in the responses of the various species to the central nervous system stimulating and cardiac sensitizing effects of Halon 1211, studies with human volunteers have been undertaken. These studies were undertaken to find the maximum concentration of Halon 1211 that could be tolerated by man for a short period of time.

Subjects exposed to 4-5% Halon 1211 did not notice any effects during the first 30 or 40 seconds of exposure, but then became dizzy and light-headed -- effects which may be likened to those of alchohol intoxication. These symptoms then increased in intensity. After one minute's exposure the dizziness was quite marked and paresthesia of the fingers and toes was also present. When exposure was continued past the point at which the symptoms became severe, one subject showed signs of stimulation of the central nervous system and a spontaneous transient disorder of the heart beat after two minutes.

Recovery on cessation of exposure was rapid when the subjects were exposed to fresh air again, and there were no after-effects, either from the first exposure or subsequent exposures.

DISCUSSION

Although Halon 1211, in common with other fire extinguishants, has some toxic properties which could be dangerous under certain circumstances, any possible risks must be balanced against the benefits of prevention of loss of life and property from the fire itself. Recommendations for the safe use of the extinguishant must therefore reflect this balance. On the basis of the various experiments described in this report, it was concluded that 4-5% Halon 1211 for one minute was the maximum that could be tolerated by man, and that amounts greater than these should be avoided. Accordingly, for total flooding systems utilizing Halon 1211 where concentrations of this order are likely, the appropriate NFPA Standard proposes that the systems should only be used in normally non-occupied areas where any personnel can leave within 30 seconds. Where concentrations of this order are not likely -- with automatic systems protecting equipment in the open, with local application systems located indoors when the volume of the fire hazard is small relative to the volume of the room, and with hand extinguishers -- these restrictions may not apply.

Experience in use has confirmed the low toxicity of Halon 1211. During the last 10 years several hundred thousand portable Halon 1211 fire extinguishers and, in more recent years, Halon 1211 total flooding systems have been used effectively without producing any adverse health effects. Thus, the advantage of Halon 1211 -- the speed with which it can attack and extinguish fires -- can be utilized with safety, and

personnel and property can be saved from the major hazards of the heat, smoke, carbon monoxide and oxygen depletion resulting from a fire situation.

REFERENCES:

1. W. H. Chambers and E. W. Krackow, "An Investigation of the Toxicity of Proposed Fire Extinguishing Fluids," U.S. Medical Division (Chemical Corps) Report No. 23, Army Chemical Center, Maryland, 1950.

2. D. L. Engibous and T. R. Torkelson, "A Study of Vaporizable Extinguishants," Wright Air Development Center Technical Report 1: 59-463, 1960.

3. R. E. Dufour, "The Life Hazards and Nature of the Products Formed When Monobromochlorodifluoromethane, Dibromodifluoromethane or Dibromotetrafluoroethane Extinguishing Agents are Applied to Fires," Underwriters' Laboratories, Inc. Report No. NC-445, 1955.

4. K. W. von Eickstedt, H. W. Paucksch and W. Höppe, "Tierexperimentelle Untersuchungen zur Akuten Toxixität von Halonen," Berufsgenossenschaff 7: 2, 1970.

5. P. S. Beck, D. G. Clark and D. J. Tinston, "The Pharmacological Actions of Bromochlorodifluoromethane (BCF) Toxicol. Appl. Pharmacol." (In Press), 1972.

6. M. B. Chenoweth and C. L. Hake, "The Smaller Halogenated Aliphatic Hydrocarbons," A Rev. Pharmacol. 2: 363, 1962.

7. D. G. Clark and D. J. Tinston, "The Influence of Fluorocarbon Propellants on the Arrhythmogenic Activities of Adrenaline and Isoprenaline," Proc. Europ. Soc. Drug Tox. 13, 1972.

8. C. F. Reinhardt, A. Azar, M. E. Maxfield, P. A. Smith and H. S. Mullins, "Cardiac Arrhythmias and Aerosol Sniffing," Arch. Environ. Health 22:265, 1971.

9. E. W. Van Stee and K. C. Back, "Short-Term Inhalation Exposure to Bromotrifluoromethane," Toxicol. Appl. Pharmacol. 15: 164, 1969.

DISCUSSION

Dr. Stewart: I would like to ask three quick questions. One, how many human subjects were exposed at the 4-5% air concentration of Halon 1211? Secondly, what was the disorder noted on one subject at two minutes? Thirdly, have you exposed human subjects to lower concentrations which produced no effect?

Dr. Clark: Regarding the first question Dr. Stewart asked -- the number of subjects we used -- we used the same three subjects, and we used them twice.

The second question -- what was the disorder of the heart beat that we saw in the subject exposed to 5%? This was one or two ventricular ectopic beats, followed by a few seconds run of ventricular tachycardia.

The third question -- have we done exposures at lower concentrations to find the no-effect level? We have not done specific experiments for this at the moment because these experiments were designed originally for assessing the safety of total flooding situations where 4 or 5% was the concentration that we were going to use.

I hope that answers the three questions.

Mr. Roberts: Could you estimate, sir, the effect of the presence of 3200 parts per million of 12B2 in one of these? To the audience, the 12B2 is a stronger agent in this area than the 1211.

Dr. Clark: The very first experiments we did were on the ordinary commercial sample of 1211, which is 99.5% pure. Our immediate sales question was it must be a toxic impurity. If you find any action in the product, it is a toxic impurity, they say. So we did other experiments to check this one out, and we got some extremely pure 1211 -- 99.9-something per cent pure -- and there were no differences in the toxic results. 12B2 or 1202 in the Halon system is certainly more toxic, but I think there is only a factor of three or four. So I don't think the presence of even a small quantity of 1202 would have influenced the results.

Mr. Spiegelman (American Insurance Association): I would like to just put this thing into a certain amount of perspective. The Underwriters' Laboratories who spoke this morning have listed two Halons, 1301, for Class A fires at concentrations of 19 and 20%. If you are to use the UL listing system on the 1301, you would be far in excess of 4, 5, 6, or 7%.

The other thing I would like to ask you about, in view of the fact that your company produces Halothane, is what other effects on the human does Halothane show, aside from the effect on the blood? Does it affect other organs? From what I have been led to understand, it does affect other organs in patients who are exposed to it, and are not encouraged to take too many exposures to Halothane or repetitive exposures.

Dr. Clark: Halothane is probably the most popular anesthetic used throughout the world today and is made by the ICI, Ltd. It is a fluorinated hydrocarbon which is related chemically to these halons that we are talking about at the moment. I think the only controversy I know about Halothane is some people say there is a possibility of slight liver damage. I think the figures they quote are possibly one in 10,000 operations where you are talking about several hours exposures. You may get some evidence of liver damage. I certainly don't know any other evidence where there is any controversy or any problem about organs being affected.

REMARKS

Mr. Wands: In keeping with the Planning Committee's concept of bringing out all of the information available on the popular halogenated fire extinguishing agents, we have made it a point to invite speakers from each of the major manufacturers to present papers at this meeting, not only to present their side of the picture, but more importantly, to present the scientific information behind the development of these products.

Our next speaker in this light is Dr. Charles F. Reinhardt from the du Pont Haskell Laboratories, who will talk to us now about the toxicology of Halon 1301.

TOXICOLOGY OF HALOGENATED FIRE EXTINGUISHING AGENTS HALON 1301 (BROMOTRIFLUOROMETHANE)

Charles F. Reinhardt and Ruth E. Reinke

E. I. du Pont de Nemours & Company

Halon 1301, bromotrifluoromethane, has been established as an excellent fire extinguishing agent. It has been used in portable extinguishers by the U.S. Army since 1959 and a portable extinguisher containing Halon 1301 has been listed by Underwriters' Laboratories, Inc. (1) since 1961. Currently, Halon 1301 is finding its widest use in total flooding systems.

Toxicity studies with Halon 1301 show that it is one of the safest of the halogenated fire extinguishing agents. In evaluating the toxicology of fire extinguishing agents, three factors must be considered:

1. toxicity of the undecomposed agent,
2. Toxicity of the thermal decomposition products of the agent, and
3. toxicity of the common products of combustion from the fire.

As the title suggests, this discussion will be limited to the first factor, namely, the toxicity of undecomposed or natural Halon 1301. The toxicology of Halon 1301 has been studied extensively by numerous laboratories and includes both animal and human inhalation studies.

ANIMAL STUDIES

The original toxicological studies on Halon 1301 were carried out in 1950 by Chambers and Krackow (2), Comstock et al. (3), and MacNamee (4) at the U.S. Army Chemical Center. They determined the approximate lethal concentration (ALC) of various fire extinguishing agents and found the ALC for Halon 1301 in rats to be 83.2 percent in air for a 15-minute exposure. Although there was evidence of edema and hemorrhage of the lungs, death probably resulted from oxygen deficiency. This low order of acute toxicity was confirmed by Dufour (5) at Underwriters' Laboratories in tests which involved four halogenated fire extinguishing agents. Guinea pigs exposed to concentrations of up to 20 percent Halon 1301 for two hours showed no significant toxic effect. On the basis of these data, Underwriters' classified Halon 1301 in Group 6 (least toxic) in their classification of life hazards.

Paulet (6) conducted toxicity studies in which rabbits, mice, guinea pigs, and rats were exposed for two hours to concentrations of Halon 1301 up to 80 percent, with the oxygen concentration maintained at 20 percent, without any mortalities. Mice exposed to concentrations of 50 to 60 percent showed central nervous system effects associated with hypoactivity. At the 80 percent level a depressant effect was noted in rats and guinea pigs while mice and rabbits showed effects associated with hyperactivity, including brief convulsions and tremors in rabbits. Subacute toxicity studies on mice, rats, and guinea pigs in which the animals were exposed to 50 percent Halon 1301, two hours a day for 15 consecutive days, resulted in no signs of toxicity.

MacFarland (7) at Hazleton Laboratories reported a study in which monkeys, rabbits, guinea pigs, and rats were exposed for two hours to Halon 1301 at concentrations of 10, 15, and 20 percent, respectively. Blood chemistry determinations performed on the monkeys revealed no abnormalities resulting from the exposure. All animals appeared normal following exposure. Pathological examination showed no evidence of gross or histopathological effect.

Comstock et al. (8) conducted a chronic study in which rats and dogs were exposed six hours daily, five days per week for 18 weeks to 2.3 percent Halon 1301. No clinical signs of toxicity were observed. On autopsy there was evidence of some diffuse congestion throughout the respiratory tract but no other noteworthy tissue changes.

Up to this point, the primary toxicological action ascribed to Halon 1301 has been its effect upon the central nervous system. However, as is characteristic of many halogenated and unsubstituted hydrocarbons, Halon 1301 would be expected to sensitize the heart to the effects of epinephrine with the production of cardiac arrhythmias. These arrhythmias are frequently ventricular in origin and may result in sudden death. This phenomenon is commonly referred to as cardiac sensitization. Several investigators have studied this aspect of Halon 1301 toxicity.

At the Hine Laboratories (9), mongrel dogs were exposed to Halon 1301 concentrations ranging from 10 to 40 percent for intervals of less than one hour after a fright-producing situation. The purpose of this experiment was to ascertain whether endogenously released epinephrine would cause ventricular fibrillation. No fatal arrhythmias occurred although central nervous system effects and shortness of breath were observed at the higher concentrations. Since the electrocardiographic activities of the dogs were not measured, it is not known whether any arrhythmias were produced. In some of the experiments, the dogs were exposed to a combination of Halon 1301 and 10 percent carbon dioxide, but, as above, no fatal arrhythmias occurred.

Van Stee and Back (10) exposed both unanesthetized and anesthetized dogs and monkeys to 10 to 80 percent Halon 1301. Most of the animals developed spontaneous cardiac arrhythmias within one to three minutes of exposure to 40 percent or more Halon 1301 but no particular consistency of response could be ascertained. The typical arrhythmic

response could, however, be elicited with the intravenous injection of 2 to 3 μg/kg epinephrine. Larger doses, 5 to 10 μg/kg, caused ventricular fibrillation with cardiac arrest in dogs. Monkeys receiving the higher doses of epinephrine were observed to have brief episodes of ventricular fibrillation but no deaths occurred. Epileptiform convulsions were seen in about 50 percent of the unanesthetized dogs exposed to 50 to 80 percent Halon 1301. Unanesthetized monkeys, on the other hand, became lethargic and no convulsions were seen. Most animals exposed to Halon 1301 while anesthetized with sodium pentobarbital exhibited an initial decrease in mean arterial blood pressure of 10 to 60 mm Hg depending on the concentration of Halon 1301.

These same investigators (11) also reported that anesthetized dogs showed a steady drop in mean arterial blood pressure and a significant fall in heart rate during exposure to 70 percent Halon 1301. Open-chested monkeys and dogs exposed to 80 percent of the agent showed a fall in systolic pressure accompanied by a slight rise in left ventricular and diastolic pressure. The authors reason that the hypotension observed with exposure to Halon 1301 results from a decrease in total peripheral vascular resistance and decreased myocardial contractility.

In experiments conducted to examine the characteristics of the cardiac arrhythmias which, as previously reported, often appeared spontaneously during exposure of monkeys to Halon 1301, Van Stee and Back (12) found that a minimal blood pressure threshold is required for their production and that the individual susceptibility to the spontaneous occurrence of arrhythmias is the result of differences in individual ability to maintain blood pressure during exposure to Halon 1301. These findings suggest that a hypertensive individual might be expected to develop arrhythmias more readily than a normo- or hypotensive one. Acidosis and epinephrine were found to decrease the blood pressure threshold required to trigger arrhythmias.

Reinhardt (13) has conducted studies in which unanesthetized dogs were exposed to either 5, 7.5, 10, 15, or 20 percent Halon 1301 for five minutes and then given an intravenous injection of 8 to 10 μg/kg epinephrine. No significant cardiac arrhythmias developed at the 5 percent level. However, at the four highest concentrations, serious arrhythmias, either multiple consecutive ventricular beats or ventricular fibrillation, were observed. The percentage of responses increased with increasing concentration of Halon 1301. One death occurred at the 10 percent level while two animals died at the 20 percent concentration. In no instance were any cardiac abnormalities noted when the animals were exposed to Halon 1301 without the injection of epinephrine. The results are summarized in Table 1.

In another series of experiments, Van Stee and Back (14) exposed rats up to five minutes to 70 to 75 percent Halon 1301 to determine the accumulation and diminution of this material in the brain, heart, and blood. Tissue samples were collected within 30 seconds after termination of each of the 1-, 2-, 3-, 4-, and 5-minute exposures or serially during the 55-minute period following the five-minute exposures. The

mean heart concentration reached 500 μg/gm of tissue. The brain concentrations of Halon 1301 were significantly higher than those of the heart at all times during exposure and reached a mean concentration of 760 μg/gm of tissue. Intracardiac blood samples showed that the concentrations of Halon 1301 in cardiac blood closely paralleled those of the heart. Only trace amounts of Halon 1301 were found in the same tissues 10 minutes post-exposure.

TABLE 1

Concentration Percent (v/v)	Number Dog Exposures	Number Marked Responses*	Percent Marked Responses
5.0	62	0	0.0
7.5	18	1	5.6
10.0	69	8	11.6
15.0	7	2	28.6
20.0	13	8	61.5

* Either multiple consecutive ventricular beats or ventricular fibrillation.

The favorable toxicity data obtained on animals suggested that Halon 1301 might have a sufficiently low order of toxicity to permit its use in environments normally occupied by man. However, since the concentration of Halon 1301 required to extinguish most fires is of the order of 5 to 6 percent, it was considered necessary to determine precisely the effects of these and somewhat higher concentrations of Halon 1301 in man.

HUMAN STUDIES

Clark (15) exposed subjects to various concentrations of Halon 1301 by means of a face mask. Exposure to 6 percent of the agent for three minutes produced slight paresthesia and very slight dizziness. There was an increase in the heart rate but otherwise there were no electrocardiographic (ECG) changes. At the 9 percent level, increasingly unpleasant dizziness caused one subject to terminate the exposure after two minutes. Again, there was an increase in heart rate but no arrhythmia. Exposures at the three highest concentrations (10, 12, and 15 percent) lasted only one minute. At the 10 percent level, slight dizziness and slight paresthesia were noted. A general rise in heart rate and blood pressure was accompanied in two subjects by depression of the T wave as noted on the ECG, but all subjects felt that continued exposure could have been tolerated. At the 12 and 15 percent concentrations, there were paresthesias and severe dizziness. All subjects showed an increased heart rate and depression of the T wave. The subjects felt that exposure continued beyond one minute would be intolerable due to dizziness and fear of losing

consciousness. Recovery occurred within one to five minutes after termination of exposure.

Reinhardt and Stopps (16) also conducted a series of human exposures. Three men were exposed twice each, in sequence to concentrations of 1, 3, 5, 7, and 10 percent Halon 1301. Each exposure lasted approximately 3 to 3-1/2 minutes. A small exposure booth measuring 2-1/2 x 3 x 5 feet was used. The desired exposure concentrations inside the chamber were achieved within ± 1/2 percent 30 seconds after the release of Halon 1301 directly into the top of the chamber.

Electrocardiograms made periodically before and continuously during each exposure showed no abnormality in any of the subjects. A force platform test for evaluation of equilibrium and a simple reaction time test in response to a visual signal were used to assess effects of the exposures on the subjects. The results of these two tests were not conclusive but suggested a slight disturbance in balance and reaction time, especially at the 7 and 10 percent levels of exposure.

All three subjects noted a characteristic subjective impression, independently described by each as a feeling of light-headedness, a feeling similar to having a couple of "stiff drinks," or as the sensation experienced just prior to unconsciousness when being given a general anesthetic. At the 7 percent level this sensation came on rapidly and then remained at a constant intensity until the exposure ended when it quickly subsided. At the 10 percent level, however, the sensation increased throughout the exposure and all three subjects felt that continued exposure might have induced unconsciousness. At the 10 percent concentration, each subject noticed a slight disturbance in his ability to respond to the visual stimulus of the reaction time device as shown by the fact that greater effort and concentration were required to make the response.

The Hine Laboratories (9) exposed 10 men, under static conditions, to 5 and 10 percent Halon 1301. In addition, the same subjects were exposed, under dynamic conditions using a Heidbrink anesthetic inhalator, to concentrations ranging from 5 to 17 percent.

The static exposures lasted 20 to 25 minutes and were conducted in a cubicle exposure chamber with an 8064-liter capacity. A battery of tests for mental alertness and muscular coordination were given during the exposures: an adjective check list for description of the subject's mental and emotional state, a modified Romberg test for evaluation of balance, a finger-to-finger test, a pursuit rotor test, and a reaction time test using three different colored lights and levers. The results of these tests at the 5 percent level were judged to indicate overall improvement in one subject, no significant changes in two, and a decrease in performance in the fourth subject; the general evaluation was that some subjects showed a minimal decrease in judgment and skill. At the 10 percent level, there was a general decrease in judgment, alertness, and neuromuscular skill. While hand steadiness was not scored, the Maze tests were revealing in that the drawn lines were wavy and irregular in all subjects at the 10 percent level in contrast to the smooth lines drawn in the control runs. The self-appraisal from the descriptive

word list showed a decrease in words describing mental acuity and alertness with an increase in words describing mild depression. Most subjects felt drowsy or light-headed and there was an increase in sense of well-being.

In the Heidbrink anesthetic inhalator tests, Halon 1301 was administered either alone or in the presence of increased carbon dioxide. Total exposure time ranged from 15 to 25 minutes. Nine subjects reported central nervous system effects; reactions were variously described as tingling, light-headedness, buzzing in the ears, and numbness or the feeling of impending unconsciousness at concentrations above 14 percent. One subject exposed up to 15.7 percent Halon 1301 reported no central nervous system effect.

Recordings of ECG, pulse, and blood pressure were made in connection with these inhalator exposures. No ECG changes were observed in seven subjects. One subject exposed to 16.9 percent Halon 1301 showed flat T waves; exposure to 14 percent Halon 1301 36 hours later resulted in cardiac arrhythmia characterized by flattening of T waves, premature ventricular contractions forming bigeminy, A-V dissociation with no pacemaker, and premature beats from various foci. Two other subjects showed ECG changes at five of the ten readings taken after exposure to 8.2 percent to 15.7 percent Halon 1301. In one case, changes were described as a lowering of the T wave on two occasions. In the other case, flattening of the T wave occurred on one occasion and increased sinus arrhythmia occurred on two other occasions. (This last subject was noted to have an initial pattern of varying T waves.) The overall tendency was towards an increased pulse and lowered blood pressure but considerable variability existed. Little, if any, cardiovascular effect was noted in those instances where the amount of inspired carbon dioxide was increased.

During and following exposure, two of the subjects reported headaches which in one case persisted for 12 hours, but otherwise recovery was prompt. The investigators concluded that Stage I anesthesia occurs at 12 to 15 percent concentrations of Halon 1301 and Stage II anesthesia would be reached at approximately 20 percent Halon 1301.

SUMMARY AND CONCLUSION

Animal experiments showed two principal toxic actions of Halon 1301: 1) stimulation or depression of the central nervous system with effects ranging from tremors and convulsions to lethargy and unconsciousness, and 2) cardiovascular effects including hypotension, decreased heart rate, and cardiac arrhythmias. Variations in both the nature and itensity of these actions existed both between species and at different concentrations of Halon 1301.

Experiments involving man clarified the nature of these target actions. The central nervous system effects are characteristic of those produced by a weak general anesthetic. To date, a state of unconsciousness has not been induced in man, either experimentally or during the use of Halon 1301. In exposures to concentrations up to 17 percent, the subjects were always sufficiently aware of their reactions to request

termination of exposure when necessary. The rapid recovery of human subjects after cessation of exposure is consistent with studies in rats indicating rapid post-exposure clearance of Halon 1301 from the brain and heart.

Human subjects exposed to Halon 1301 have shown both an increase and decrease in blood pressure and heart rate as well. The apparent intrinsic pharmacological tendency of this agent to induce hypotension is undoubtedly modified in many instances by endogenous epinephrine released in response to stimulation of the central nervous system. In addition, human subjects have developed spontaneous electrocardiographic changes including one instance of a definite cardiac arrhythmia when exposed to relatively high concentrations of Halon 1301.

The data supplied by three separate human studies indicate that concentrations of Halon 1301 exceeding 10 percent may prodice definite cardiac and central nervous system effects and that concentrations of the order of 15 to 20 percent may lead to unconsciousness and conceivably death. On the other hand, no cardiac effects and only negligible central nervous system effects would be expected to occur at concentrations not exceeding 7 percent Halon 1301 for exposures five minutes or less in duration. No significant adverse health effects have been reported from Halon 1301 in more than 10 years of practical use as a fire extinguishant.

On the basis of the toxicity data presently available, it is concluded that Halon 1301 is safe for use in total flooding systems where personnel are normally present provided the concentrations and conditions of egress conform to those prescribed in the National Fire Protection Association 12A standard on Halogenated Fire Extinguishing Agent Systems - Halon 1301 (17). Currently, Halon 1301 is not recommended for use as an inerting agent in normally occupied areas.

In conclusion, it must be emphasized that some degree of risk is generally attendant upon the use of chemical extinguishing agents, and Halon 1301 is no exception. It does have toxic properties which could be dangerous under certain circumstances. However, the toxicity of the agent must be put in perspective, and any risk must be balanced against the benefits. The prompt extinguishing action of Halon 1301 minimizes the formation of pyrolysis products from the agent itself as well as the major hazards of a conflagration; namely, smoke, heat, carbon monoxide formation and oxygen depletion. These latter hazards far outweigh any due to the extinguishant itself. It is therefore of paramount importance that the fire be detected and extinguished quickly after inception.

REFERENCES:

1. Underwriters' Laboratories, Inc., National Board of Fire Underwriters, "Report on Liquefied Gas Extinguishers, Assignment 59161490," The Fire Guard Corporation, Northbrook, Ill. (Unpublished), 1961.

2. W. H. Chambers and E. H. Krackow, "An Investigation of the Toxicity of Fire Extinguishing Liquids. Part I. Summary," Medical Division Research Report No. 23, Chemical Corps, Army Chemical Center, Md., 1950.

3. C. C. Comstock, F. P. McGrath, S. B. Goldberg and L. H. Lawson, "An Investigation of the Toxicity of Proposed Fire Extinguishing Fluids. Part II. The Approximate Lethal Concentration to Rats by Inhalation of Vapors for 15 Minutes," Medical Division Research Report No. 23, Chemical Corps, Army Chemical Center, Md., 1950.

4. J. K. MacNamee, "An Investigation of the Toxicity of Proposed Fire Extinguishing Fluids. Part III. The Pathology in Rats Produced by Inhalation of Proposed Fire Extinguishing Fluids," Medical Division Research Report No. 23, Chemical Corps, Army Chemical Center, Md., 1950.

5. R. E. Dufour, "The Life Hazards and Nature of the Products Formed When Monobromomonochlorodifluoromethane ('Freon 12B1'), Dibromodifluoromethane ('Freon 12B2'), Monobromotrifluoromethane ('Freon 13B1'), or Dibromotetrafluoroethane ('Freon 114B2') Extinguishing Agents are Applied to Fires," Underwriters' Laboratories, Inc., Report No. NC-445, Chicago, Ill. (Unpublished Report dated March 10, 1955, amending letters dated May 1, May 2, and May 31, 1957), 1955.

6. G. Paulet, "Etude Toxicologique et Physiopathologique du Monobromo-Trifluoromethane (CF_3Br)," Arch. Mal. Prof. Med. Trav. Secur. Soc. 23: 341-348 (Chem. Abstr. 60: 7358e), 1962.

7. H. N. MacFarland, "Acute Inhalation Exposure - Monkeys, Rabbits, Guinea Pigs and Rats - 'Freon' 1301," Final Report, Hazleton Laboratories, Inc., Falls Church, Va. (Unpublished), 1967.

8. C. C. Comstock, J. Kerschner and F. W. Oberst, "Toxicology of Inhaled Trifluoromonobromomethane and Difluorodibromomethane Vapors from Subacute and Chromic Exposures of Rats and Dogs," Medical Laboratories Research Report No. 180, Army Chemical Center, Md., (ASTIA, AD 11563), 1953.

9. The Hine Laboratories, Inc., "Clinical Toxicologic Studies on 'Freon' FE 1301," Report No. 1, San Francisco, Cal. (Unpublished), 1968.

10. E. W. Van Stee and K. C. Back, "Short-term Inhalation Exposure to Bromotrifluoromethane," Toxicol. Appl. Pharmacol. 15:164-174, 1969.

11. E. W. Van Stee and K. C. Back, "Hypotension During Bromotrifluoromethane Exposure," U.S. Clearinghouse Fed. Sci. Tech. Inform., AD 731549(AMRL-TR-68-182), 1971.

12. E. W. Van St and K. C. Back, "Spontaneous Cardiac Arrhythmias Induced by Bromotrifluoromethane," U.S. Clearinghouse Fed. Sci. Tech. Inform., AD 723645(AMRL-TR-68-188), 1971.

13. C. F. Reinhardt, "Cardiac Arrhythmias Induced by Epinephrine During Inhalation of Certain Halogenated Hydrocarbons," E. I. du Pont de Nemours & Company, Haskell Laboratory for Toxicology and Industrial Medicine, Report No. 14-69, Newark, Del. (Unpublished), 1969.

14. E. W. VanStee and K. C. Back, "Brain and Heart Accumulation of Bromotrifluoromethane," U.S. Clearinghouse Fed. Sci. Tech. Inform., AD 721211(AMRL-TR-70-139), 1971.

15. D. G. Clark, "The Toxicity of Bromotrifluoromethane (FE1301) in Animals and Man," Imperial Chemical Industries Ltd., Industrial Hygiene Research Laboratories, Cheshire, England. (Unpublished Report), 1970.

16. C. F. Reinhardt and G. J. Stopps, "Human Exposures to Bromotrifluoromethane," E. I. du Pont de Nemours & Company, Haskell Laboratory for Toxicology and Industrial Medicine, Report No. 230-66, Newark, Del. (Unpublished), 1966.

17. National Fire Protection Association, "Halogenated Fire Extinguishing Agent Systems - Halon 1301," NFPA No. 12A-1971, Boston, Mass., 1971.

ADDITIONAL REFERENCES:

K. C. Back and A. A. Thomas, "Aerospace Problems in Pharmacology and Toxicology," Annu. Rev. Pharmacol. 10:395-412, 1970.

V. L. Carter, Jr., K. C. Back and D. Farrer, "The Effect of Bromotrifluoromethane on Operant Behavior in Monkeys," Toxicol. Appl. Pharmacol. 17:648-655, 1970.

P. M. Chikos, Jr., E. W. Van Stee and K. C. Back, "Central Nervous System Effects of Bromotrifluoromethane," U.S. Clearinghouse Fed. Sci. Tec. Inform., AD 710442(AMRL-TR-69-130, Paper No. 6), 1969.

J. W. Clayton, Jr., "The Mammalian Toxicology of Organic Compounds Containing Fluorine," Handbuch Exp. Pharmakol. 20:459-500, 1966.

J. W. Clayton, Jr., "Fluorocarbon Toxicity and Biological Action," Fluorine Chem. Rev. 1:197-252, 1967.

C. C. Comstock and F. W. Oberst, "Comparative Inhalation Toxicities of Four Halogenated Hydrocarbons to Rats and Mice in the Presence of Gasoline Fires," A. M. A. Arch. Ind. Hyg. Occupational Med. 7:157-167, 1953.

E. I. du Pont de Nemours & Company, "Toxicology of du Pont FE 1301 Fire Extinguishing Agent," "Freon" Products Division, Bulletin S-35A, Wilmington, Del., 1971.

D. L. Engibous and T. R. Torkelson, "A Study of Vaporizable Extinguishants," U.S. Clearinghouse Fed. Sci. Tech. Inform. PB161942 (WADC Technical Report 59-463), 1960.

J. C. Gage, "The Acute Toxicities of Chlorobromomethane, Trifluorobromomethane, Difluorodibromomethane, and Tetrafluorodibromoethane," Imperial Chemical Industries, Ltd., Industrial Hygiene Research Laboratories, Report No. IHR/54, Welwyn, Herts, England (Unpublished), 1954.

E. Gross, "Die Toxizität einiger Halogenkohlenwasserstoffe die als Feuerlöschmittel sur Diskussion stehen," VFDB Z. 15:96-98, 130-135 (Chem. Abstr. 67:25224x), 1966.

R. A. Rhoden and K. L. Gabriel, "Some Effects of $CBrF_3$ Inhalation on Myocardial Glycolysis," Paper read at Tenth Annual Meeting of the Society of Toxicology, March 7-11, 1971, Washington, D. C. (Abstract, Toxicol. Appl. Pharmacol. 19:410), 1971.

R. A. Rhoden and K. L. Gabriel, "Effects of $CBrF_3$ Inhalation and Epinephrine Challenge on Certain Myocardial Metabolite Levels," Paper read at American Industrial Hygiene Conference, May 24-28, Toronto, Canada, 1971.

J. Scholz and W. Weigand, "Toxikologische Untersuchungen an Trifluormonobrommethan," Zentr. Arbeitsmed. Arbeitsschutz 14:129-131 (Chem. Abstr. 62:2166h), 1964.

E. W. Van Stee, "Some Aspects of the Pharmacology of Bromotrifluoromethane," Ph.D. dissertation, Ohio State University, Columbus, Ohio (Diss. Abstr. Int. B 31:4238-4239), 1970.

E. W. Van Stee, K. C. Back and R. B. Prynn, "Alteration of the Electroencephalogram During Bromotrifluoromethane Exposure," Toxicol. Appl. Pharmacol. 16:779-785, 1970.

DISCUSSION

Mr. Wood: My question perhaps relates to all three of these papers. I noted in the case of 70 to 80 percent concentrations that the mixture must have been with oxygen. Otherwise the oxygen deficiency would have been present. In the case of the lower concentrations, such as 5 to 20 percent, was there oxygen enrichment to compensate or were these with as little as 16 percent oxygen, which would correspond to about a 20 percent mixture? In other words, in the lower concentrations, 20 percent and below, was the oxygen enriched to compensate and make it a normal oxygen concentration? If not, could some of these effects be partly attributable to oxygen deficiency?

Dr. Reinhardt: In the studies which we carried out, we did not add oxygen at those lower levels. However, I think the control studies would

serve to take care of that if the oxygen was a factor. It would show up. I think your point is well taken, but at that level I am not sure that even that decrease would have a significant effect. Maybe someone else in the room could comment on it.

Dr. Clark: I could make a quick comment on that last one as regards oxygen tension falling. If you think of normal aircraft cabins, they are pressurized at about 8,000 feet, which is equivalent to 16 percent oxygen at sea level. I have never really noticed any problem of unconsciousness when I have been flying.

Mr. Roberts: I would like to focus on the experimental method. It seemed that I noticed that at the 7 percent level producing light dizziness from your chamber, and comparing that to the fact that a mask which was used in the work by Dr. Clark produced that same light dizziness at 6 percent. That is a considerable difference when we are talking about 5 percent being the level of the margin of safety for use.

Dr. Reinhardt: Assuming that the subject is getting the proper aeration, I don't think that the way it is administered in that regard would be a factor. I would also comment that even though this may be important to those who design systems, when you are doing human exposures and testing humans, the response is variable enough that if you see a little bit of difference between 5, 6 or 7 percent, that is really not that significant in terms of human response. I think this is what you might expect as a biological variation. These effects which were described by the various authors really are not that different. They are all similar qualitatively. There is a very minor quantitative difference.

Mr. Hanbury: I have a problem with some of these agents that we are discussing as to general nature. We are discussing experiments with people who are in real good physical shape and so forth. I am hoping from this conference to get some information which I can extrapolate to people generally who may have problems of heart conditions, they may be drinkers, they may take drugs of some type, and the effect of these agents against these types of conditions. I would appreciate any explanation that you could give me. I am laboring under the impression that if people are drinkers and so forth, they can be affected more by these halons than not. I would like some guidance in this area.

Dr. Reinhardt: As far as drinkers are concerned, someone who has an effect from alcohol, this would certainly be additive, and you would expect a more serious effect. However, you get into an area where, say, people with cardiac disease and who are taking other drugs, this is kind of an unknown area. It certainly is one that probably needs further study. However, on the basis of the fact that these materials do produce arrhythmias or may produce arrhythmias, certainly anyone who would have a history of cardiac arrhythmia might be more susceptible to the effects of these materials. To go beyond that, I don't think we have the information at this time.

Mr. Wards: Can you relate the concentrations of 1301 and the injection levels of epinephrine to normal fire-fighting conditions for 1301, the

concentrations needed for fire control, and also the endogenous levels of epinephrine which might be present in a human being during a period of excitement?

Dr. Reinhardt: As you saw in the studies which we conducted with our dogs, we did have cardiac effects at the 7.5 percent level and above. However, these animals received large intravenous injections of epinephrine, and these levels are probably of the order of 10 times greater than the maximum amount that man may secrete under stress. We feel that there is probably a very wide margin of safety here, although we can't put an actual number on it.

Mr. Wands: And the level of 1301 for normal fire control purposes?

Dr. Reinhardt: Excuse me, it is 5 to 6 percent.

Dr. Rozniecki: On the effects at low levels on humans, in the three studies that you mentioned, were they all double blind, single blind, or mixed exposures?

Dr. Reinhardt: In these particular studies, I don't know that any of them were double blind studies. I can only answer for sure for ours, and it was not. At that time this was kind of an unknown area to us, and we were proceeding rather cautiously. So we started with the lower levels and worked up. We had highly trained subjects, though, so we figured that this would not be so much a factor with them.

From the Floor: Would someone explain "double blind?"

Dr. Reinhardt: I am not sure I am the best one, but I think it means when neither the subject nor the investigator knows what is being administered.

Mr. Wands: Dr. Back, do you want to comment on that?

Dr. Back: Yes. It is impossible to make this double blind, because the agents have an odor. So the guy knows he is getting it, but not how much.

REMARKS

Mr. Wands: We are very fortunate this afternoon to have Dr. Nicola Rainaldi from Montecantini-Edison in Italy to talk to us now about Halon 2402.

APPRAISAL OF HALOGENATED FIRE EXTINGUISHING AGENTS

Nicola Rainaldi

Montecatini-Edison, Italy

This report refers to experimental searches already done or under way in the laboratories of Montecatini-Edison concerning Halon 2402 applications in the fire-fighting field.

Beginning in 1966, our main goal was to find a fire-fighting agent which could exhibit the following performance (Table 1):

TABLE 1

Requirements for an "Ideal" Fire Extinguishing Agent

1. High effectiveness on Class A, B, and C fires,
2. Liquid at ambient temperature but readily vaporized on the flames,
3. High density,
4. Low toxicity rating.

These properties would allow the agent to be used with favorable results either in enclosures with total flooding systems or outdoors against large fires. Being a liquid, at room temperature, handling and storage problems would be more easily solved.

A first screening on several halons pointed to Halon 2402 (1, 2 dibromo-tetrafluoro ethane). Its physical properties, which are shown in Table 2, meet the requirements of Nos. 2 and 3 above. The results of its extinguishing effectiveness, measured by laboratory tests (Creitz's method and Explosion Burette), are shown in Table 3. Later, controlled practical tests on different sized fires, both indoor and outdoor, proved the validity of this choice (Table 4). Note that the discharge times are significantly low and, in the case of the extinguishment by total flooding technique, the required agent concentration ranges between one and two percent by volume (100 - 200 gm/cu.m.).

TABLE 2

Properties of Halon 2402

Boiling Point	117°F
Freezing Point	- 168°F
Vapor Pressure	
at 77°F	6.6 psia
at 122°F	16.0 psia
Density of Liquid	135 lb./cu. ft.
Dielectric Strength (Vapor)	4.2 (Nitrogen = 1.0)
Resistivity of Liquid	10^{11} Ohm - cm
Evaporation Rate	116 (Ether = 100)
Surface Tension	18 dynes/ cm
Corrosion of Metals:	
Iron	0.0086 mils/year
Stainless Steel	nill
Brass	nill
Aluminum	nill
Copper	0.0018 mils/year

However, the toxicity rate of the agent itself had to be more deeply investigated and also the toxicity caused by its thermal decomposition products during fire extinguishment. The literature data were neither sufficient nor exhaustive. Furthermore, the purity level of the agent was never mentioned or taken into consideration for toxicity ratings.

The experimental investigations were planned bearing in mind the practical application conditions. The tests were run in consecutive steps ranging from laboratory tests on animals to tests, again on animals, but performed in practical fire-fighting conditions. The study to evaluate the physiological effects of Halon 2402 on humans was obviously subordinated to favorable results in the above tests.

TABLE 3

Effectiveness of Halon 2402

(Laboratory Results)

Flame Suppression Data by Creitz

Fuel	Quantity to Extinguish
Acetone	1.22%
Benzene	1.29%
Methane	0.80%
Exane	1.46%
Virgin Naphta	1.53%

Flammability Peak Data by "Explosion Burette"

Fuel	Requirement for Explosion Suppres.
Acetone	2.4%
Benzene	2.5%
Methane	0.8%
n-Exane	3.5%

ANIMAL STUDIES

Table 5 shows the results of a study on the acute toxicity in Sprague Dawley male rats having an average weight of 250 gms., which were carried out according to the plan proposed by the Committee on Toxicology of the National Academy of Sciences, National Research Council of the U.S.A. (1). These data allow classification of Halon 2402 as a relatively harmless substance in accordance with the classification of Hodge and Sterner (2).

It can be observed that the ALD_0 value of 13.1% is eight to ten times higher than the concentrations normally used to extinguish indoor fires by the total flooding technique.

TABLE 4

A) Ground Fires

Fuel	Fire Surface	Extinguishing Time	Agent Used
		60 sec. after prebur.	
Gasoline	4 sqmt	2 sec.	2.0 Kg.
Gasoline	6 sqmt	3 sec.	6.0 Kg.
J F 4	64 sqmt	30 sec.	74.0 Kg.

B) Fires in Enclosed Volumes

Fuel	Extinguishant		
	Discharge Time	Kg. Used	% by Volume
Acetone	6.5 sec.	6.5	1.25
Benzene	4.5 sec.	4.5	.86
Gasoline	5.5 sec.	5.5	1.05
Transformer Oil	5.5 sec.	5.5	1.05
Foamed Polystirene	7.0 sec.	7.0	1.33
Rubber Fires	7.0 sec.	7.0	1.33

Note: Preburning time 30 sec.

TUBE TESTING

The toxicity studies on thermal decomposition of Halon 2402 were preceded by a kinetic investigation of the thermal stability of the agent. This test series, performed in a heated tube, aimed to evaluate the influence of some chemical and physical parameters, such as agent contact time, tube material, and temperature on the rate of decomposition itself.

The pyrolysis data obtained in these experiments are shown in Table 6 and have led to the following considerations:

1. The rate of decomposition is strongly affected by the temperature and the wall material which comes in contact with the agent.

2. The thermal decomposition rate is greater with metal walls than with inert walls such as the test run on the quartz tube, especially at lower temperatures.

3. The decomposition products are mainly CO, C_2F_6 and oxidizing products such as bromine and, not to be excluded, carbonyl halides. According to our opinion this method of measuring thermal stability of halons is not realistic because it does not take into consideration two basic parameters being present in fire-fighting conditions.

a. The fuel which can change the whole dynamics of halon decomposition.

b. The humidity deriving from the combustion which favors the formation of hydrogen halides in respect to the free halogens -- the former are much less toxic than the latter.

4. Therefore, it was necessary to find the real trend of agent behavior in flame extinguishment with reference to the agent contact time at actual temperatures present in a fire.

TABLE 5

Acute Toxicity of Halon 2402 (Montedison)

	By Inhalation 4 Hr. Exposure	By Endoperitone UM
A.L.D. 0	131.000 ppm (1.4 gm/ lt)	0.50 gm/ Kg.
A.L.D. 50	173.000 ppm (1.8 gm/ lt)	6.48 gm/ Kg.
A.L.D. 100	216.0000 (2.3 gm/lt)	12.0 gm/ Kg.

Sprague Dawley male rats have been used.

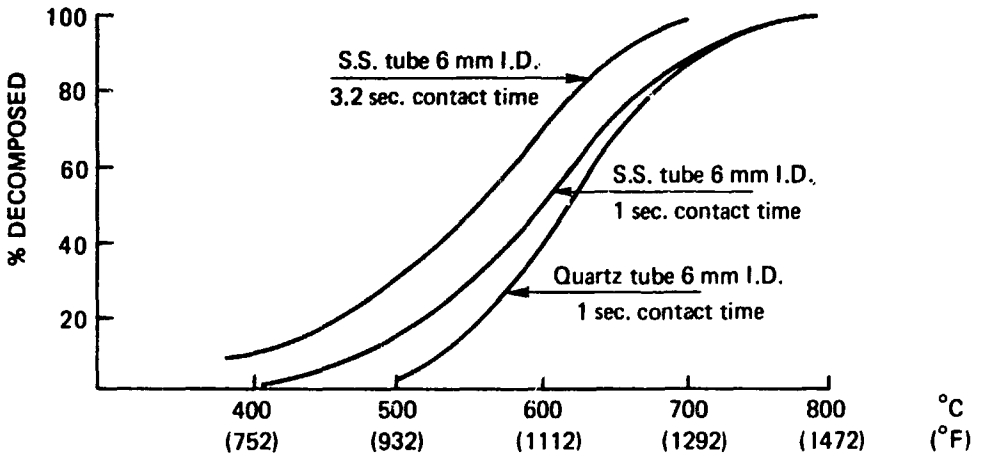
Narcosis Data

(4 Hr. Exposure)

Narcosis: 500 - 1000 gm/ cumt

TABLE 6

Thermal Stability of Halon 2402



T (°C)	S.S. Tube % Decomposed		Quartz Tube % Decomposed
	1 sec.	3.2 sec	1 sec.
400	7	10	0
500	10	20	2
550	28	54	11
600	45	69	28
650	74	88	76
700	84	99	90
750	97	100	98
800	100	100	100

METAL PLATE TESTS

In order to obtain information on the amount of decomposition of Halon 2402 in practical use conditions, extinguishing tests were run in the presence of metal plate. The experiments were run in a box of 45 cu. m. volume with concrete walls on the floor of which a 0.4 sq. m. iron pan was situated, shielded by three metal plates (Table 7) fitted with thermocouples. The extinguishing agent was sprayed from a nozzle mounted on the ceiling having a flow rate of 1000 gr/sec. Analysis of samples taken from the internal atmosphere, after the extinguishment, have shown that the amount of agent decomposed was much less than the amount observed running the pyrolysis in a tube. The decomposition rate, as measured by HF produced, ranged approximately from 0.3 to 2.5% of the agent used, and depended upon the preburn time and the nature of metal plates (aluminum or iron) for an extinguishing time of six to seven seconds. In addition, it should be observed that several minutes are required before the temperature of the plates is high enough to cause any appreciable decomposition.

ANIMAL FIRE-EXTINGUISHING TESTS

Being aware of the substantial difference of the trend between the decomposition rates obtained from a heated tube and from realistic fire extinguishing conditions, practical experimentations were planned at Milano University as well as on a larger scale at our laboratories in cooperation with Milano University. The former test (Table 8) was performed by extinguishing a small hexane fire by direct spray of the agent inside a metal box where some animals were placed. These experiments were repeated in a chamber of 20 cu. m. volume, on the floor of which a 0.1 sq. m. pan containing 250 cu. cm. of fuel was placed. Extinguishment was either by the total flooding technique or by directing the agent streams of a portable extinguisher onto the flames which yielded the following observations (Table 9):

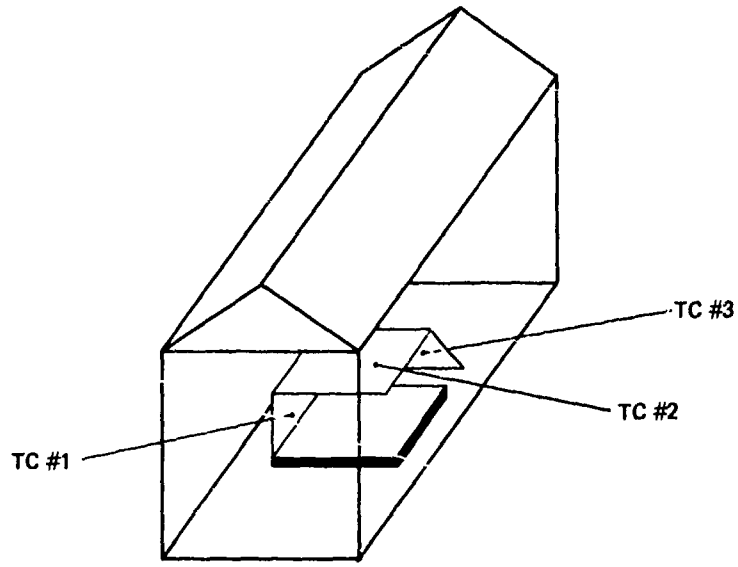
1. The amount of decomposition products depends upon the discharge time -- the higher the rate of discharge, the lower the decomposition level.

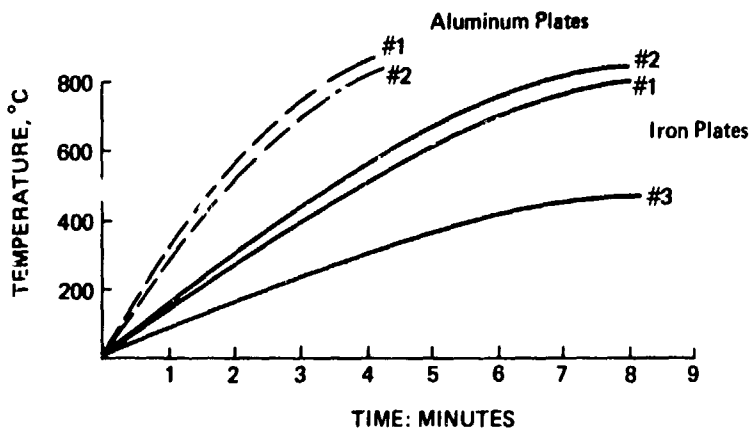
2. Free bromine and carbonyl halides have been detected,but at levels greatly lower than those from the pyrolysis tube.

3. Among the products in the chamber, the CO level was found to be very high when extinguishment was performed at low discharge rates. For example, during experiment No. 5, with a very slow discharge, the mortality was one rat and five guinea pigs. Histological examination showed that their deaths were caused by CO.

4. During experiments Nos. 1, 2, 6 and 7, where the flames were put out by fast extinguishment, none of the animals exposed to the decomposition products died. Note that experiment No. 6 was identical to experiment No. 5 except for discharge time.

TABLE 7





Plates	Preburn. Time sec	Temperature (°C)		Agent Discharged	Br^- ppm	HF ppm
		Initial	Final			
Iron	120	1-330 2-150 3-350	330 270 380	1.24%	5	55
Aluminum	120	1-500 2-420	380 330	1.44%	10	120

TABLE 8

Results of the Study on the Acute Toxicity in Rats of the Decomposition Products by Pyrolysis of Halon 2402

Experimental Data

Animal Used	10 Male Sprague Dawley Rats
Exposure Box	1.92 cu mt.
Fuel	50 cc n-Exane in a Pan Ø 18 cm
Extinguishing Technique	Direct Spray

Experiment	Concentration Determined in the Box						Temperature on the Box °C		Mortality Within 14 Days
	Halon 2402 % by vol.	Br^- ppm	COBr ppm	F* mg/l	F* ppm	CO ppm	Before Fire	After Fire	
Ignition of 50 cc Exane (70 sec. burning time)	--	-	-	-	-	180	22	65	0/10
n-Exane Fire Extinguished by 28 g. Halon 2402	1.29	-	56	5	4.[illegible]	1200	22	44	0/10

Preburn Time: 30"

F* - Hydrolyzable Fluorine

TABLE 9

Toxicity Study in a 20 cu mt Concrete Box

Run	Extinguishment	Fuel	Agent Used gr.	Concentration in the Box HBr mg/lt	Br_2 mg/lt	F + mg/lt	COX_2 PPm	CO % v/v	Mortality Within 14 Days
1	Hand Fast (1 sec.)	Exane	205	-	-	-	< 0.25	0.01	0/20
2	Hand Fast (1 sec.)	Methanol	215	0.04	-	0.01	< 0.25	0.02	0.20
3	Hand Slow (10 sec.)	Exane	205	-	0.06	0.04	0.5	0.03	3/10
4	Hand Slow (10 sec.)	Methanol	215	0.44	0.44	0.11	1.0	0.1	2/10
5	Total Flooding Slow (15 sec.)	Exane	3200	0.38	0.92	0.25	2.5	2.0	6/10
6	Total Flooding Fast (1.5 sec.)	Exane	3200	-	-	-	< 0.25	-	0/10
7	Total Flooding Fast (1.8 sec.)	Methanol	8800	-	-	-	< 0.25	-	0/10

F + Total Fluorine determined as HF

From the above experiments, it might be reasonable to conclude that the toxicity of the undecomposed halon had to be taken into consideration because:

1. The low amounts of decomposition products produced during fire extinguishment with fast discharge.

2. The combustion products themselves may reach dangerous concentrations.

HUMAN STUDIES

With this assumption, and because of the low concentration required to extinguish the flames, we plan to carry out the experimental study on the physiological effects of Halon 2402 on humans. Being aware of the nature of such experiments, the study is being prepared in two stages.

Stage No. 1 -- The tests will examine the human behavior at low concentrations for a long exposure time in order to ascertain whether measurable physiological effects occur and whether any of them are serious.

Stage No. 2 -- The tests will examine human behavior at concentrations in the range of those designed for total flooding systems, but at low exposure times in the range of 30 - 90 seconds to allow people to leave the [illegible]sed area where discharge (purposely or acc[illegible]lly) occurs.

As results from this program are available, they will be published.

REFERENCES:

1. Committee on Toxicology, National Research Council, "Principles and Procedures for Evaluating the Toxicity of Household Substances," Publ. No. 1138, National Academy of Sciences, Washington, D.C., 1964.

2. H. C. Hodge and J. H. Sterner, "Tabulation of Toxicity Classes," Am. Ind. Hyg. Assoc. Quart., 10:93-96, 1949.

DISCUSSION

Mr. Wands: In the last slide where you showed the animals exposed to the fire and the combustion products during the extinguishment, how quickly were the animals removed from the test chamber?

Dr. Rainaldi: The exposure time for these animals was 15 minutes, and they were then removed from the experimental chamber, and submitted to observation for the following 14 days.

REMARKS

Mr. Wands: This afternoon we are going to continue with our toxicology discussion, except that this time instead of talking about specific compounds, we are going to talk about some of the principles, mechanisms, some of these problems that the hydrogenated hydrocarbons present. I think I should caution you, if you have not already become aware of it, that the life style of a toxicologist, I guess you would say, is to push his experimental animals to the limit in order that he may identify the potential problems for human beings. That means that you will frequently see things like mortality data, you will see pulmonary edema, and fancy words like these that may or may not mean something to some of you, but they carry a certain degree of emotional response, a certain amount of fright and impact to them, and these are not necessarily related to the real world of fire fighting. I think if you will be patient with us throughout the rest of this afternoon and through tomorrow that the total overall impression you will carry away from the symposium will be one of perspective. That is our intent and our hope in planning this program as an appraisal of these materials. We hope to look at their pros and their cons, potential problems, and put these into perspective of the choice to fry or not to fry. We do hope that the two days will be fruitful in that direction.

Our next speaker this afternoon is Dr. Kenneth Back from the Aeromedical Research Laboratories at Wright-Patterson Air Force Base.

CARDIOVASCULAR AND NERVOUS SYSTEM EFFECTS OF BROMOTRIFLUOROMETHANE: A SHORT REVIEW

Kenneth C. Back and Ethard W. Van Stee

Aerospace Medical Research Laboratory

The United States Air Force has acquired an intense interest in the development and up-dating of chemical fire extinguishing agents and systems. Designs range from fully automated fire protection systems to hand-held portable fire extinguishers. This paper will review pertinent experiments performed to assess the toxic hazards associated with the use of $CBrF_3$ and to come to some understanding of the mechanisms of its pharmacodynamic activities.

In the first experiments, we studied the effects of breathing mixtures of 10 to 80 percent $CBrF_3$ mixed with oxygen on dogs, monkeys and baboons (1).

Twelve beagle dogs (five males, seven females) 18-30 months of age which weighed 7.8-12.4 kg, four young adult female monkeys (Macaca mulatta) which weighed 4.6-6.1 kg, and two female baboons (Papio sp.) which weighed 10.0 and 12.5 kg were exposed to 10, 20, 30, 40, 50, 60, 70 or 80 percent bromotrifluoromethane ($CBrF_3$) in oxygen.

Conscious monkeys were restrained in a chair device. Dogs were restrained in a ventilated box of our own design in the normal ventrum-down posture of a reclining dog.

Five of the 12 dogs and all four monkeys were exposed to $CBrF_3$ while conscious. All the animals used were exposed to $CBrF_3$ while anesthetized. A majority of the exposures were to concentrations greater than 40 percent $CBrF_3$. At least two exposures at each concentration from 10 to 80 percent were performed on at least five dogs and three monkeys in both the conscious and anesthetized states. The baboons were exposed only to 50-80 percent $CBrF_3$.

Two dogs under pentobarbital anesthesia were exposed to an 80 percent mixture of $CBrF_3$ on O_2 for 35 and 40 minutes, respectively. The intravenous injection of 10 μg/kg of epinephrine resulted in ventricular fibrillation and cardiac arrest in both animals (Figure 1).

The general response of the dog to nonlethal exposures of $CBrF_3$ consisted of a cardiovascular effect and a central nervous system effect. All the central nervous manifestations of $CBrF_3$ toxicity which were observed in the conscious dog were eliminated by the induction of Stage III Plane I pentobarbital anesthesia. At least some alteration

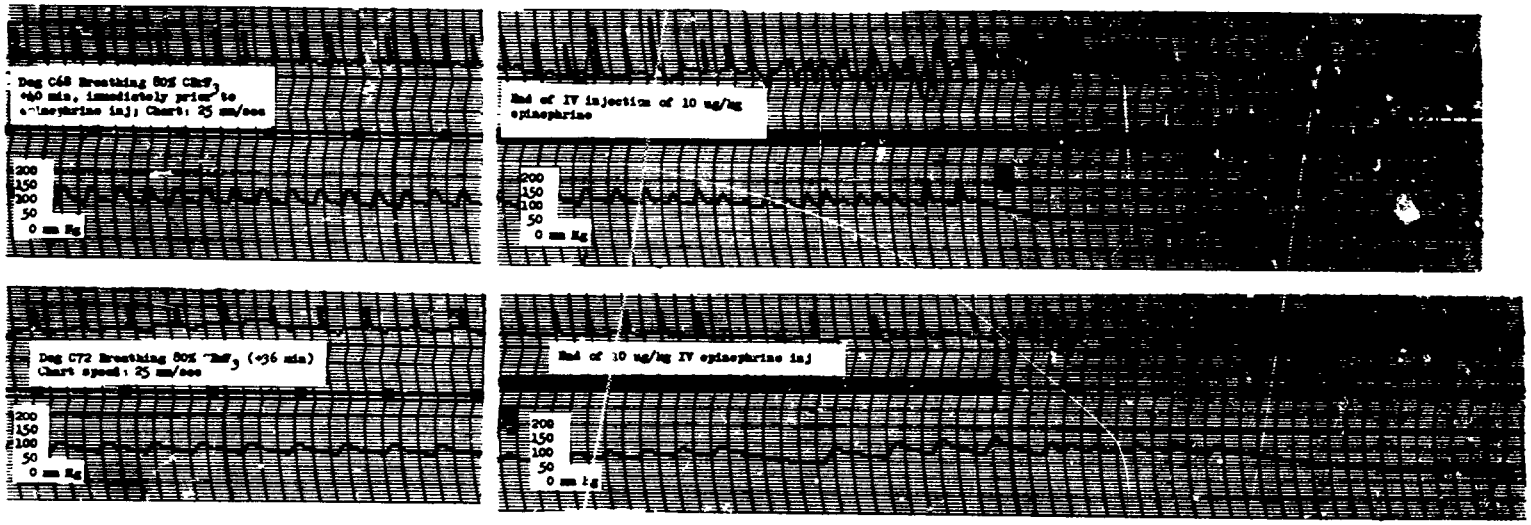


FIGURE 1. Electrocardiogram (lead II) and central arterial blood pressure recordings from two dogs exposed to bromotrifluoromethane immediately before and during the intravenous injection of ten μg/kg of epinephrine which show the onset of ventricular fibrillation and subsequent cardiac arrest.

of cardiovascular function was seen in all dogs in all experiments whether conscious or anesthetized when the dogs were exposed to 20-30 percent or greater $CBrF_3$ levels.

The heart rate was irregularly increased by 10-15 percent from resting rates of 67-100 beats/min during the first several seconds of breathing 20-30 percent $CBrF_3$. The increase in heart rate was definite and regularly reproducible when the dogs were exposed to 40 percent or higher $CBrF_3$ concentrations. When arrhythmias appeared, which usually began at 15-120 seconds after starting the exposure to $CBrF_3$, a simple tachycardia became impossible to distinguish.

An increase in heart rate accompanied by some degree of hypotension was studied most extensively while the dogs were breathing the 50 percent or 80 percent mixture. The blood pressure fall varied from 20 to 60 mmHg. The pulse pressure was decreased by 0-30 mmHg from an average normal of 40-55 mmHg.

The changes in heart rate, blood pressure, and pulse pressure reversed when an animal exposed to $CBrF_3$ was switched to room air. Recovery required approximately twice as long as development.

Figure 2 illustrates the results of a typical experiment in which an anesthetized dog was allowed to respire spontaneously a 50 percent mixture of $CBrF_3$. The most striking response to the $CBrF_3$ was the rapidly changing blood pressure. The heart rate changed irregularly with cardiac output generally varying directly with heart rate. Peripheral vascular resistance was lowered during exposure to $CBrF_3$. Determinations of cardiac output and calculation of total peripheral vascular resistance during the $CBrF_3$ exposures were performed after two to three minutes of exposure and at the end of six-minute exposures. Exposure to 50 percent $CBrF_3$ did not affect pulse pressure during the relatively short periods of these experiments. Longer exposures produced a gradual decrease in pulse pressure over a period of 25-30 minutes. Pulse pressure decreased more rapidly when the gas mixture contained 80 percent $CBrF_3$.

Four of the nine conscious dogs exposed to $CBrF_3$ had epileptiform convulsions of 10-30 second duration. The convulsions were characterized by generalized rigidity, apnea, and cyanosis of the tongue. The only apparent residual effects were an elevation in body temperature and fatigue which was associated with the muscular effort of the convulsion. Convulsions were precipitated with two to five successive exposures within a period of an hour. When exposed to 80 percent $CBrF_3$, the onset of the convulsions took place within three to four minutes. The length of exposure which was required to precipitate the convulsions was greater at lower concentrations of $CBrF_3$. Convulsions appeared after 12-minute exposure to 50 percent $CBrF_3$, the lowest concentration which caused convulsions after any length of exposure under 40 minutes. The dogs that did not develop convulsions showed the same general signs as those that convulsed. Dogs exposed to 20 percent or greater concentrations of $CBrF_3$ became visibly agitated within one to two minutes. The severity of the agitation increased with the concentrations of

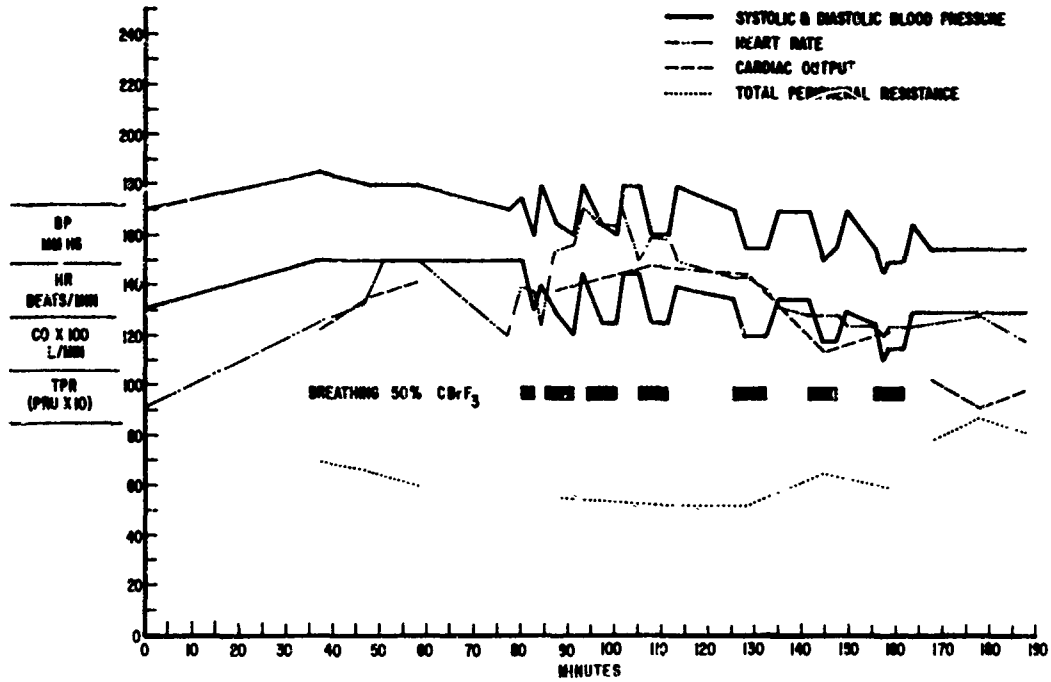


FIGURE 2. Results of an experiment in which a dog under pentobarbital anesthesia was exposed to 50% bromotrifluoromethane intermittently. During these periods a significant hypotension was seen which was reversed immediately upon removal of the $CBrF_3$.

$CBrF_3$. The dogs looked about the room apprehensively. Within one to three minutes generalized muscular tremors (shivering) could be distinguished. Episodes of shivering lasted a few seconds and recurred every five to twenty seconds. General anesthesia induced by pentobarbital or thiamylal blocked all central nervous system signs.

The responses of the monkeys and baboons to $CBrF_3$ were very similar.

Two monkeys and both baboons were exposed to 80 percent $CBrF_3$ under pentobarbital anesthesia for ten minutes or more. The intravenous injection of ten μg/kg of epinephrine produced little significant alteration of the ECG. Although brief episodes of ventricular fibrillation were observed, no deaths occurred.

The general responses of the primates to $CBrF_3$ bore many similarities to those of the dog. The cardiovascular response was similar to that of the dog except that cardiac arrest could not be induced with large doses of epinephrine during exposure to the compound. The central nervous response was markedly different from that of the dog.

All four monkeys which were exposed to $CBrF_3$ while conscious exhibited signs of cortical depression in contradistinction to the

agitation exhibited by dogs. Shivering was observed in monkeys exposed to $CBrF_3$. This was accompanied by tranquilization of the normally aggressive behavior of macaques. Their eyelids remained half-closed and they refused to bare the teeth or bite. They remained conscious, however, and showed enough interest in orange juice to swallow a few drops when offered.

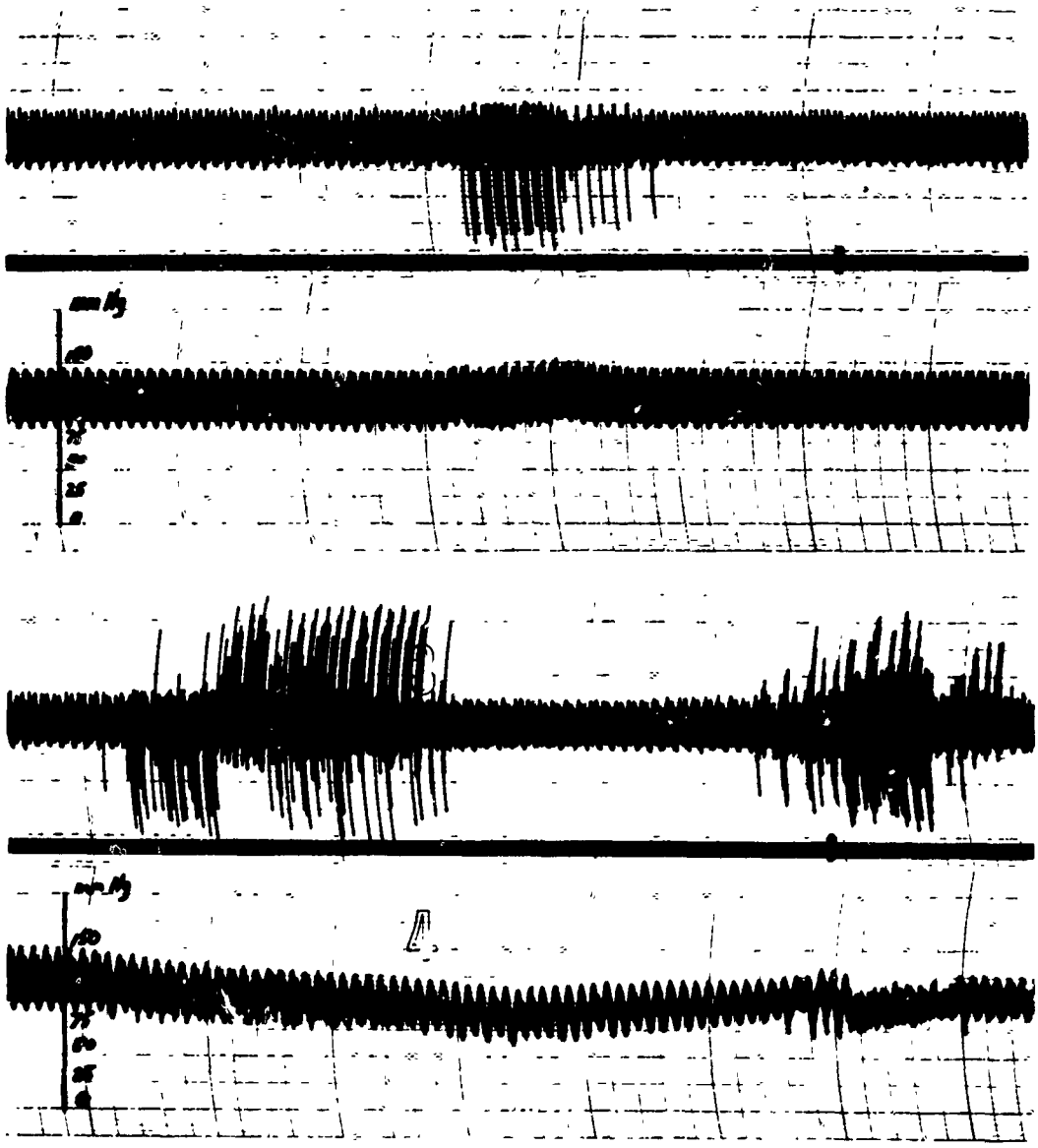


FIGURE 3. The occurrence of cardiac arrhythmias depended on the maintenance of a minimal blood pressure. Arrhythmias were triggered by raising the blood pressure by the intravenous infusion of epinephrine (upper tracing). Arrhythmias also were abolished and restored by the alteration of blood pressure by exsanguination and reinfusion (lower tracing).

The next group of experiments was designed to examine the characteristics of the cardiac arrhythmias which often appeared spontaneously during exposure of animals to $CBrF_3$ (2).

Eight monkeys (Macaca mulatta) from two to four years old and weighing 2.5 to 5.0 kg were used. A single group of five of the monkeys was used for three different experiments. Animals were anesthetized with intravenous four percent pentobarbital sodium. An initial dose of 30 mg/kg was given and subsequent small injections were given to maintain Stage III, Plane 1 anesthesia. Femoral arterial and venous catheters were inserted. Endotracheal catheters were inserted and connected to a Harvard respiration pump and the monkeys were ventilated at 9 to 16 cpm. Arterial blood samples were obtained throughout the experiments at approximately 30-minute intervals and pH, P_{CO_2} determined.

During the first experiment (control) arterial blood pH was regulated between 7.35 and 7.45 with 100 percent O_2 at ten respiratory cycles per minute by adjusting tidal volume. During the second experiment (acidosis) the arterial blood pH was regulated between 7.10 and 7.30 with oxygen to which was added zero to five percent CO_2. The animals were ventilated at nine respiratory cycles per minute and a tidal volume of not less than 25 ml/kg. During the third experiment (alkalosis) the arterial blood pH was regulated between 7.50 and 7.80 with 100 percent O_2. The animals were ventilated at 12 to 16 respiratory cycles per minute and a tidal volume of about 35 ml/kg.

The animals were observed for 30 to 60 minutes in the control, acidotic, or alkalotic state and then exposed to 10, 20, 30, 40, 50, 60, 70 and 80 percent $CBrF_3$ in O_2 (or O_2 and CO_2) for ten-minute periods in succession. Electrocardiogram Lead II was monitored on a Grass direct-writing electrocardiograph. Arrhythmias resulting from ventricular ectopic pacemaker formation appeared spontaneously during the first five minutes of exposure to 30 percent or greater concentrations of $CBrF_3$. When the arrhythmias appeared the arterial blood pressure, monitored using a Statham pressure transducer, was lowered by bleeding from a vein. The blood pressure was lowered until the arrhythmias were abolished; then the blood was reinfused which returned the blood pressure to normal and caused the reappearance of the arrhythmias (Figure 3, lower tracing). Exsanguination and reinfusion were performed at each concentration of $CBrF_3$ from 30 to 80 percent. The successive exposures were performed twice on each animal during each experiment, providing four arterial blood pressure values at which arrhythmias were abolished or reappeared for each animal, at each concentration, and in each acid-base state. Arterial blood pressure in most cases was not high enough to trigger arrhythmias spontaneously at $CBrF_3$ concentrations of 10 and 20 percent. During these exposures epinephrine was infused to raise the blood pressure to levels high enough to trigger arrhythmias (Figure 4, upper tracing).

The data, in brief, on the acid-base balance experiments show that acidosis decreased the threshold for arrhythmias and alkalosis increased the threshold at concentrations of 10 to 20 percent $CBrF_3$ but were without effect at concentrations greater than 30 percent.

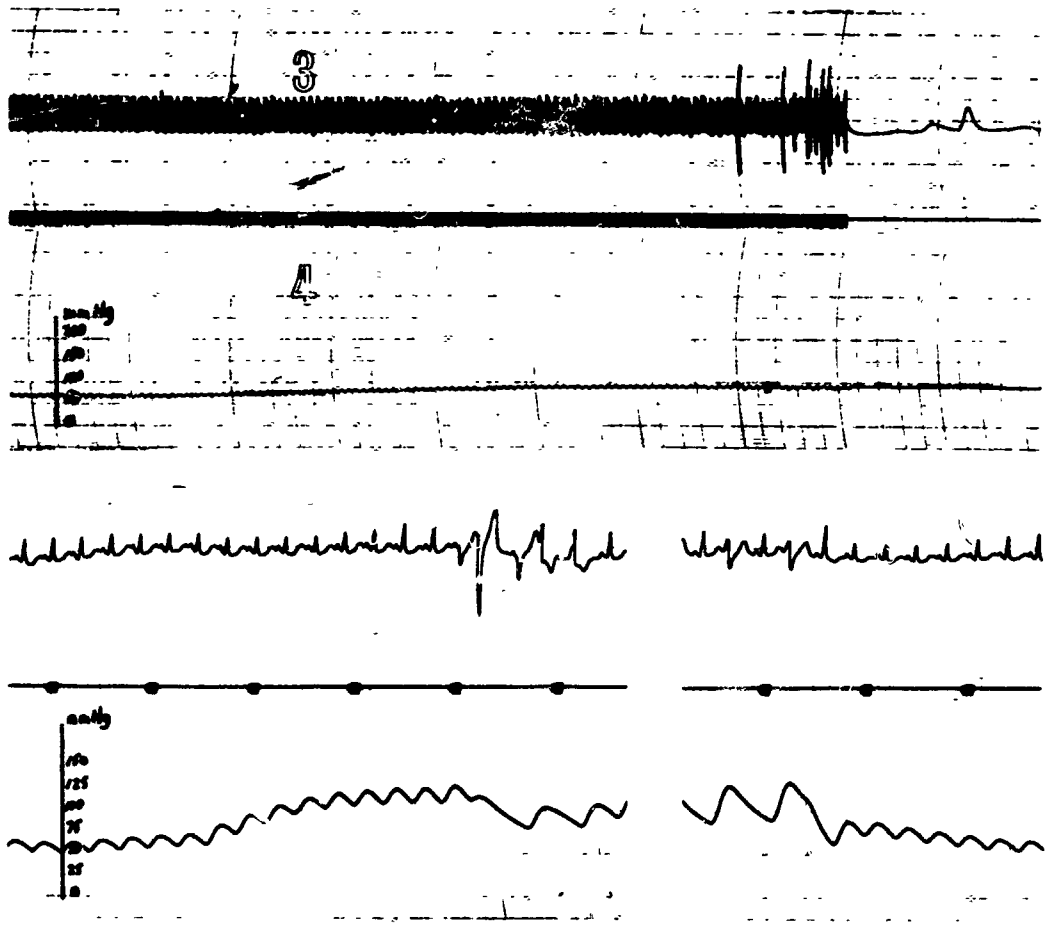


FIGURE 4. The upper tracing illustrates the triggering of arrhythmias in a monkey exposed to 70 percent $CBrF_3$ by the expansion of plasma volume with six percent dextran. The lower tracing illustrates the triggering and abolition of arrhythmias during exposure to 70 percent $CBrF_3$ by constriction and release, respectively, of the thoracic aorta.

The upper tracing of Figure 4 illustrates how the arrhythmias were induced by the expansion of the plasma volume with six percent dextran to raise blood pressure. The lower tracing of Figure 4 shows the development of arrhythmias by aortic constriction to raise blood pressure. The arrhythmias were abolished following release of the aortic constriction.

In another group of experiments using anesthetized dogs, it was found that exposure to 70 percent $CBrF_3$ produced a fall in total arterial blood pressure without a significant decrease in cardiac output which indicated a fall in peripheral resistance (3). Experiments with open-chested animals indicated that $CBrF_3$ reduced myocardial contractility as evidenced by a rise in left ventricular end diastolic pressure (Figure 5).

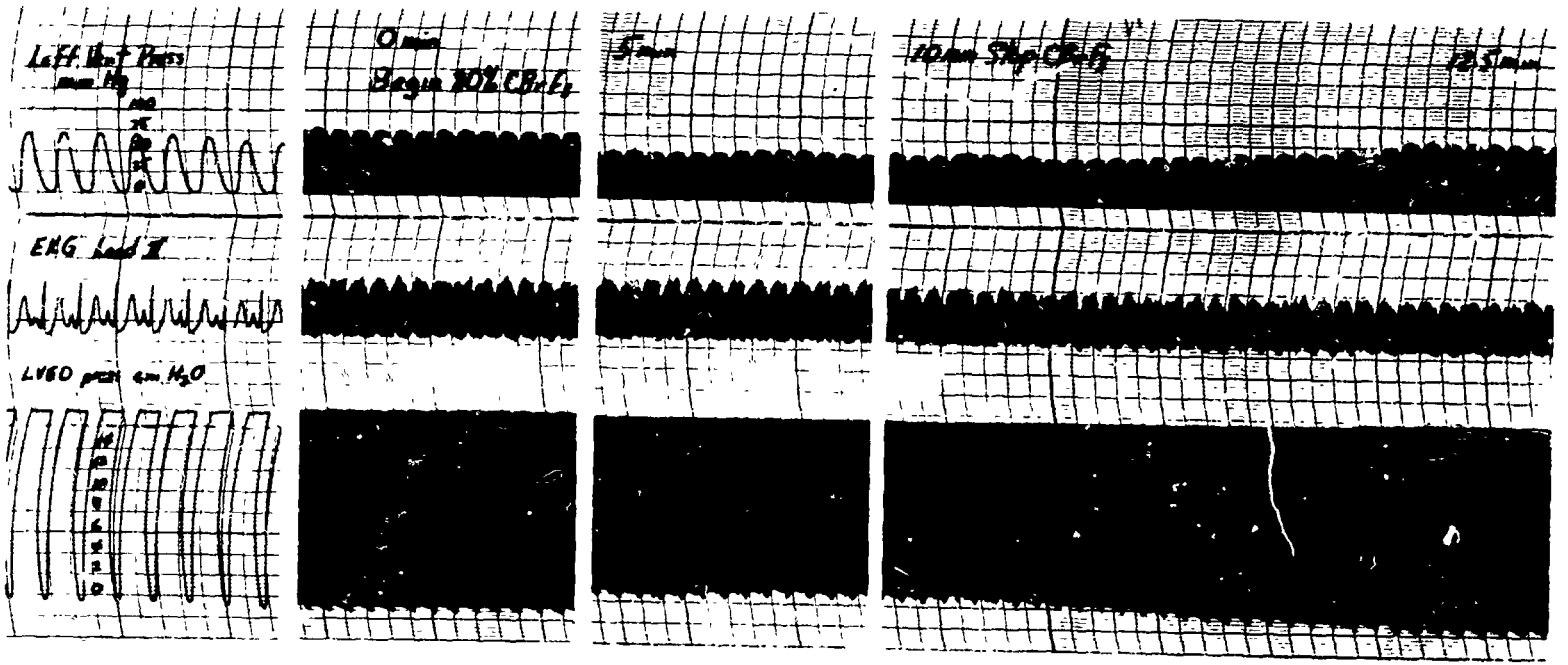


FIGURE 5. Effect of $CBrF_3$ exposure on left ventricular blood pressure in the open-chested monkey. The top tracing shows the fall in systolic blood pressure during $CBrF_3$ exposure. The bottom tracing shows the same ventricular pressure curve amplified to show the rise in left ventricular and diastolic (LVED) pressure (systolic pressure is not shown in the bottom tracing).

The next set of experiments were designed to determine the cause or causes of blood pressure changes during exposure to $CBrF_3$.

The purpose of the first group of experiments described hereafter was to determine if 1) the blood pressure decrease was the result of a peripheral vascular resistance change. If so, 2) was the peripheral vascular resistance change the result of a direct vascular smooth muscle effect, a neurogenic vasomotor effect, or a combination of the two? The purpose of the second set of experiments 3) was to determine if exposure to $CBrF_3$ significantly impaired ganglionic transmission (4).

Thirty-seven male beagles weighing from 7.7 to 13.6 kg were selected. They were free from obvious diseases, defects, and parasites. They were housed in individual cages and maintained on a standard laboratory diet and water ad libitum. Food was withheld for 24 hours prior to the experiment.

Blood was cross-matched for each pair of the 32 dogs selected for the 16 cross-circulation experiments.

The dogs used in the cross-circulation experiments were anesthetized with a single intravenous dose of thiamylal sodium (18 mg/kg in four percent solution). Endotracheal and venous catheters were inserted. Immobilization was maintained by the continuous intravenous infusion of ten percent alpha-chloralose in polyethylene glycol (PEG-200) at a nominal rate of 20 mg/kg/hr. Cutdown sites were infiltrated subcutaneously with 0.5 percent lidocaine hydrochloride prior to surgery.

The dogs were ventilated mechanically at a tidal volume of 125 ml and rate of 14-18 cycles per minute. Respiratory rate was regulated manually throughout the experiments in order to maintain arterial blood pH between 7.35 and 7.45 and P_{CO_2} between 35 and 42 torr. Blood gas and pH determinations were made with a blood gas analyzer.

Polyethylene catheters were inserted into a brachial artery of each dog. The catheters were attached to pressure transducers and recordings made on a direct-writing recorder.

A polyethylene catheter was advanced to the level of the abdominal aorta through a femoral artery of one of the dogs (donor). The catheter was attached to a length of vinyl tubing that passed through the finger mechanism of a constant-flow perfusion pump. The outflow end of the pump tubing contained a bubble trap and a "T" for attachment to a pressure transducer. The end of the tubing was connected to a polyethylene catheter that was inserted in a peripheral direction two cm into a femoral artery of the other dog (recipient). The venous effluent was returned to the donor by gravitation through polyethylene catheters leading from the femoral vein of the perfused hind limb (HL) of the recipient to the post cava of the donor via a femoral vein of the donor. The extracorporeal circuit was filled with cross-matched blood from a third donor. A tight nylon ligature was placed around the perfused hind limb as high on the leg as possible to minimize the mixing of the circulations. The perfusion rate was regulated between 8.0 and 15.5 ml/min

to establish a control pressure that approximated the arterial blood pressure of the recipient.

Twenty to 30 mg of sodium heparin was given to the donor intravenously.

The perfused leg temperature was maintained with hot water bottles and thermal insulation.

The donor was ventilated with 100 percent O_2 at all times except when it was being exposed to a fluorocarbon mixture. The recipient was ventilated with air between exposures.

Mixtures of about 70 percent (67-70 percent) bromotrifluoromethane (99.7 percent purity) in O_2 were made by flowing the respective gases into a mixing bag volumetrically. Exposure of the dogs was performed by attaching a hose from the mixing bag to the appropriate respiration pump inlet.

Electrocardiograms (Lead II) were recorded from each dog throughout the experiments (Figure 6).

The dogs used in the ganglionic transmission experiments were given subcutaneous injections of 1.5 ml of a mixture of 0.4 mg/ml fentanyl and 20 mg/ml droperiodol. Thirty minutes later an intravenous injection of ten mg/kg of pentobarbital sodium was given followed by fractional doses of pentobarbital sufficient to maintain light surgical anesthesia (Plane 1, Stage III). Arterial blood pressure was monitored as described for the previous set of experiments. Nictitating membrane tension was determined using a force displacement transducer attached to the membrane with a silk thread.

Following anesthetization the right vagosympathetic trunk was transected and silver wire electrodes from a constant voltage stimulator were attached to the central and peripheral cut ends of the trunk. Ten-second trains of 5 v, 100 Hz, 1 msec, biphasic pulses were delivered to the central cut end and five-second, 5-10 v, 100 Hz, 1 msec, biphasic pulses were delivered to the peripheral cut end at the appropriate times during the experiment.

The experiment was designed with a pre-exposure control period, an exposure period, and a postexposure period. The animals were exposed to 80 percent $CBrF_3$ in O_2 for 40-78 minutes during the exposure period and to air at other times. During the consecutive periods the following determinations were performed.

At intervals of three to five minutes, three trains of electrical stimuli were applied first to the central and then to the peripheral cut ends of the vagosympathetic trunk. Nictitating membrane tension was recorded during electrical stimulation of the central cut end of the vagosympathetic trunk and blood pressure was recorded during the other procedure. Recordings were obtained prior to exposure, during exposure (beginning not before ten minutes of exposure to the $CBrF_3$) and postexposure (beginning not before 30 minutes postexposure).

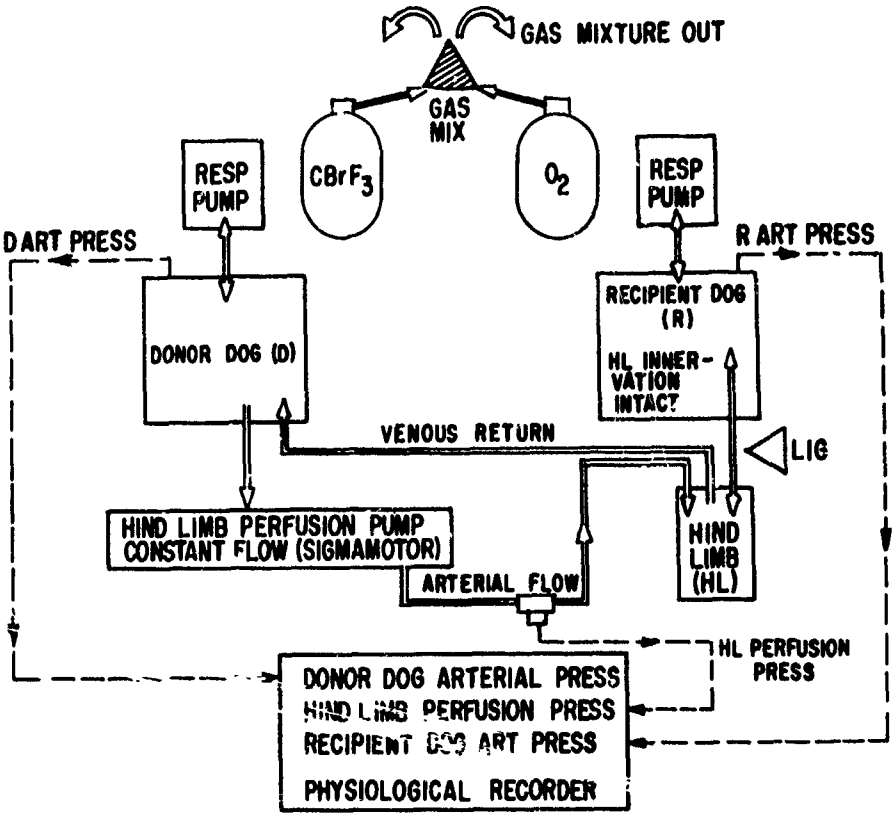


FIGURE 6. Schematic diagram of cross-circulation experiments. Arterial blood from the donor was pumped at constant flow through the hind limb of the recipient. The normal innervation of the HL remained intact. $CBrF_3$ and O_2 were mixed (7:3 v/v) and administered to the respective dogs by way of the respiration pump inlets.

The results of the cross-circulation experiments are as follows. Exposure of the donor (Figure 7) to $CBrF_3$ was accompanied by an average decrease in mean arterial blood pressure of 31 torr. Four of the 16 donor dogs were pretreated with reserpine which greatly attenuated their hypotensive response to $CBrF_3$ and observations made on these animals were not included in these calculations. The mean perfusion pressure of the recipient HL was unchanged by the exposure of the donor to $CBrF_3$.

Exposure of the recipient (Figure 8), on the other hand, resulted in not only an average decrease of 25 torr in the recipient mean arterial blood pressure, but also an average decrease of 22 torr in the HL mean perfusion pressure.

The decrease in the HL perfusion pressure during $CBrF_3$ exposure of the recipient was largely abolished by the pretreatment of the HL with phenoxybenzamine (Figures 10 and 11), a treatment that was without a significant effect on the recipient systemic arterial blood pressure decrease during the exposure. Pretreatment of the recipient with hexamethonium completely abolished the pressure change responses in both the recipient mean arterial and HL mean perfusion pressures (Figure 9).

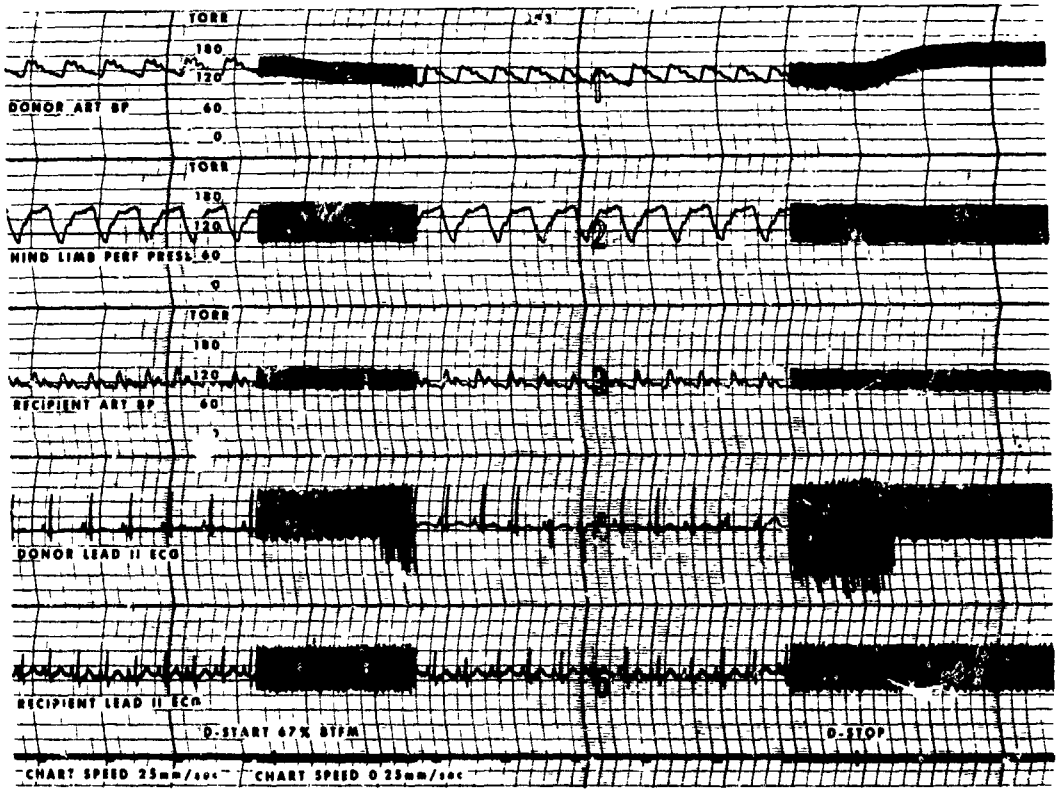


FIGURE 7. Donor arterial, hind limb perfusion, and recipient arterial blood pressures were recorded during the exposure of the donor to 67 percent $CBrF_3$ (BTFM). The beginning and end of the exposure are represente by the first two vertical marks on the bottom line. Donor arterial blood pressure decreased during exposure to $CBrF_3$. Hind limb perfusion pressure remained unchanged. These results suggest that $CBrF_3$ had no direct effect on vascular smooth muscle and no other effect that would result in the liberation of significant amounts vasodilatory humoral agents locally in the peripheral vascular bed or remotely into the general circulation. Evidence for PVCs that occurred during the exposure may be seen in donor lead II ECG (Van Stee and Back, 1969).

Results of the ganglionic transmission experiments are as follows. Figure 12 illustrates the effect of exposure to 80 percent $CBrF_3$ on membrane nictitans tension (M.N. Tension) during constant electrical stimulation of the central cut end of the vagosympathetic trunk (sympathetic innervation of the M.N. via the superior cervical ganglion). Tension is given in arbitrary units. Tension was reduced by 40 percent or more during the exposure. The tension returned to pre-exposure values after 30 minutes postexposure.

Figure 13 illustrates the effect of exposure to $CBrF_3$ on vagal inhibition of the heart. Prior to exposure the stimulus was adjusted to just produce a brief cardiac arrest followed by escape from

the vagal inhibition. The identical stimulus was subsequently applied during exposure and postexposure. Vagal inhibition was shown to be significantly reduced during the period of $CBrF_3$ exposure and to return to control values postexposure.

A few words concerning the effects of $CBrF_3$ on the central nervous systems other than outward signs of intoxication, as shown by convulsions in dogs or loss of aggressiveness in conscious monkeys, are in order. In dogs and monkeys immobilized with tubocurarine and exposed to 70-80 percent $CBrF_3$, the most significant findings were dominance of the EEG's by 6-9 HZ waves beginning two to three minutes after exposure, and a nearly normal susceptibility of the EEG to activation by auditory

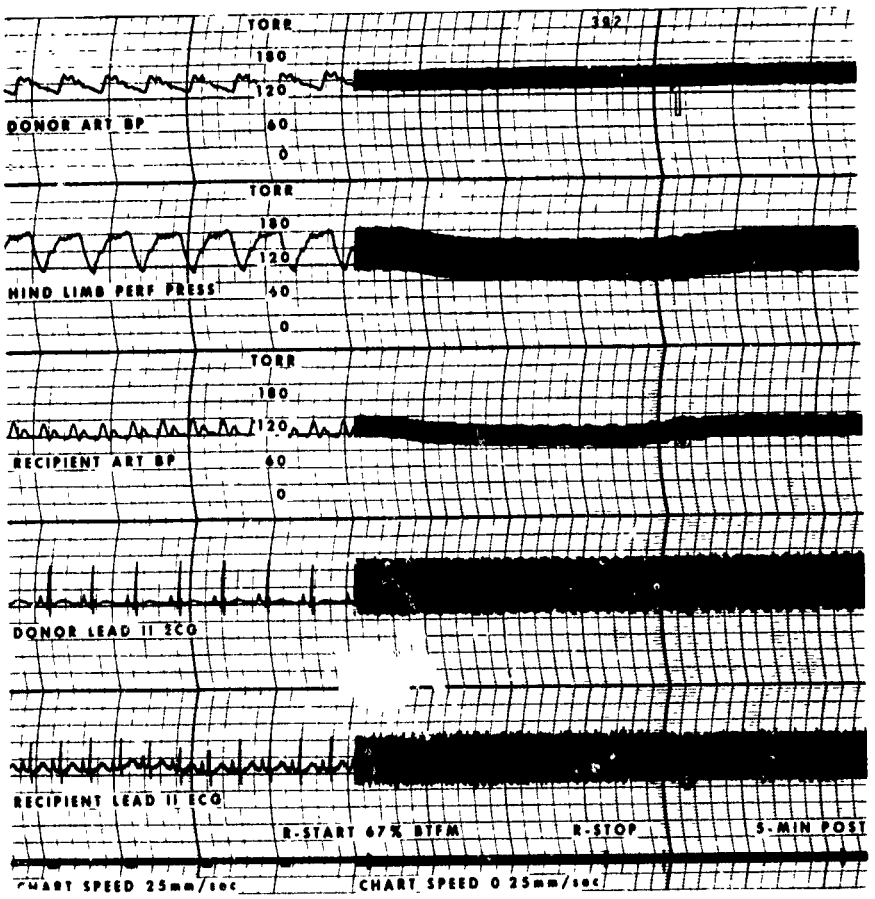


FIGURE 8. Donor arterial, hind limb perfusion, and recipient arterial blood pressures were recorded during the exposure of the recipient to 67 percent $CBrF_3$ (BTFM). The beginning and end of the exposure are represented by the first two vertical marks on the bottom line. Donor arterial blood pressure remained unchanged during the exposure. HL perfusion and recipient arterial pressures decreased simultaneously during the exposure. These results suggest that $CBrF_3$ caused a decrease in vasoconstrictor tone.

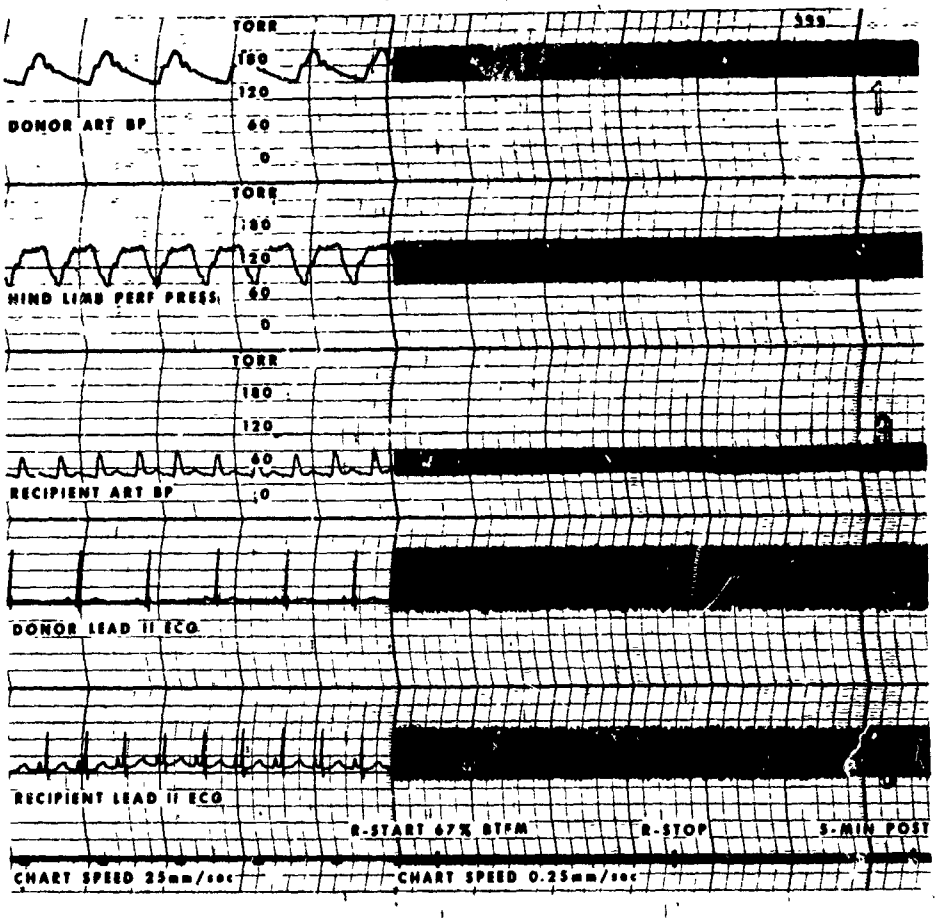


FIGURE 9. Donor arterial, hind limb perfusion, and recipient arterial blood pressures were recorded during exposure of the recipient to 67 percent $CBrF_3$ (BTFM) following treatment of the recipient with ten $\mu g/kg$ of hexamethonium. The beginning and end of the exposure are represented by the first two vertical marks on the bottom line. All three pressures remained unchanged during the exposure. These results suggest that in the absence of vasoconstrictor tone no further decrease in peripheral vascular resistance occurs during exposure to $CBrF_3$.

and photic stimuli. This is different than during anesthetic exposure to halothane (5).

In another group of experiments, Chikos et al. presented data to support the hypothesis that $CBrF_3$ produces cortical depression with relative sparing of the reticular activating system, permitting alterations in performance without loss of consciousness in the monkey (6).

Carter et al. reported on the effects of $CBrF_3$ on performance in trained monkeys. Seven monkeys trained on continuous and discrete avoidance performance tasks were exposed to concentrations of $CBrF_3$ ranging from 10.5 to 42.0 percent. Significant performance decrements

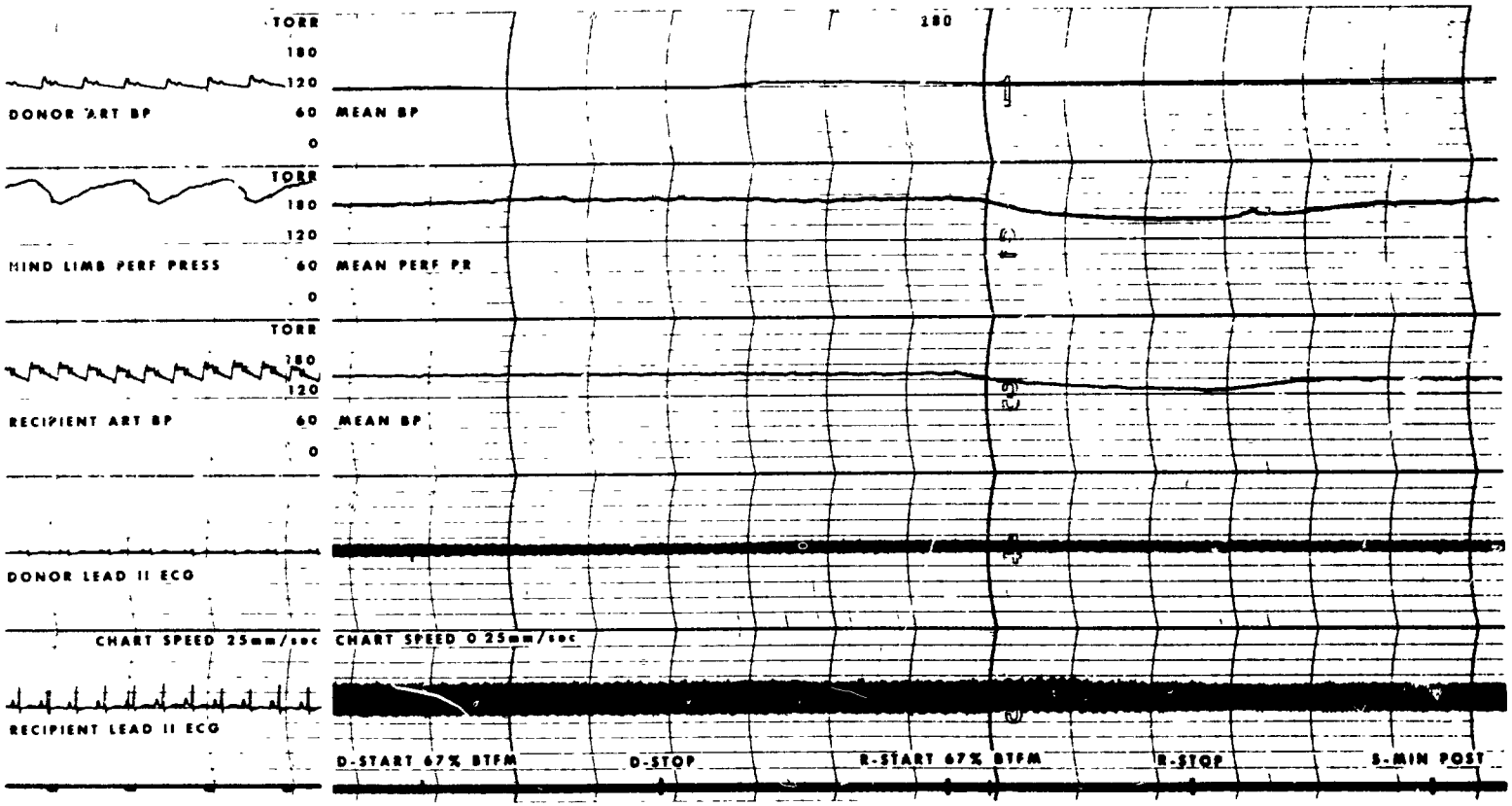


FIGURE 10. Donor arterial, hind limb perfusion, and recipient arterial blood pressures were recorded during exposure of first the donor, and then the recipient, to 67 percent $CBrF_3$ (BTFM). The periods of exposure are represented by the vertical marks on the bottom line. Donor mean arterial blood pressure decreased during exposure of the donor and hind limb perfusion and recipient arterial mean pressures decreased during exposure of the recipient.

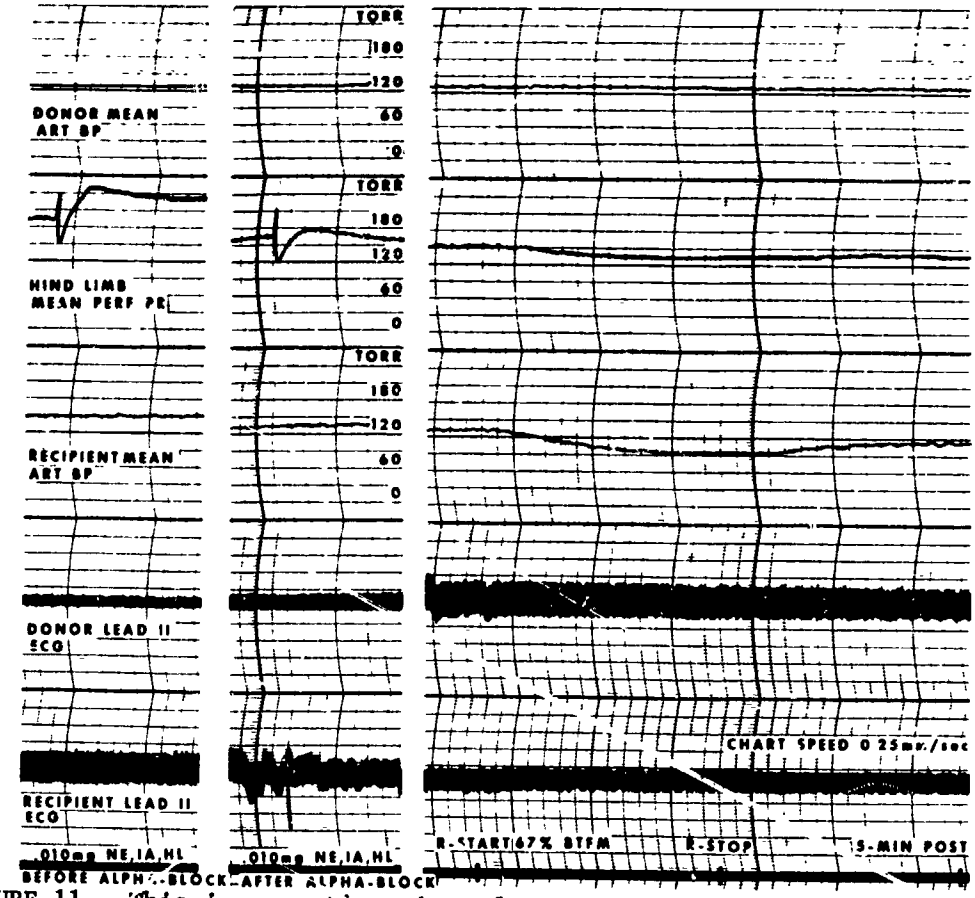


FIGURE 11. This is a continuation of Figure 10. The hind limb mean pressure responses to the hind limb intraarterial injection of ten μg of norepinephrine shown in the first two panels before and after treatment of the hind limb with phenoxybenzamine. The third panel shows that the hind limb perfusion pressure decrease was markedly attentuated during exposure of the recipient to 67 percent $CBrF_3$ (BTFM) as compared to a similar exposure represented in Figure 10.

were observed in all subjects during exposures of 20-25 percent $CBrF_3$. Higher concentrations resulted in impaired performance to the point of complete disruption of operant behavior in some subjects. No visible signs of central nervous system depression or analgesia accompanied this loss of ability to perform on conditioned performance tasks. These results suggest that the mechanism by which $CBrF_3$ causes impaired performance differs from the central nervous system depression and analgesia produced by halogenated anesthetics (7).

We have performed some experiments on two other compounds; namely, F2402 and F1211 for comparative purposes. Preliminary screening of F1211 ($CBrClF_2$) for cardiovascular effects has been completed in two sets of experiments with repeated observations within each experimental setup. Although this sample size is not large enough for a definitive statement of the cardiovascular consequences of F1211 exposure, the technics

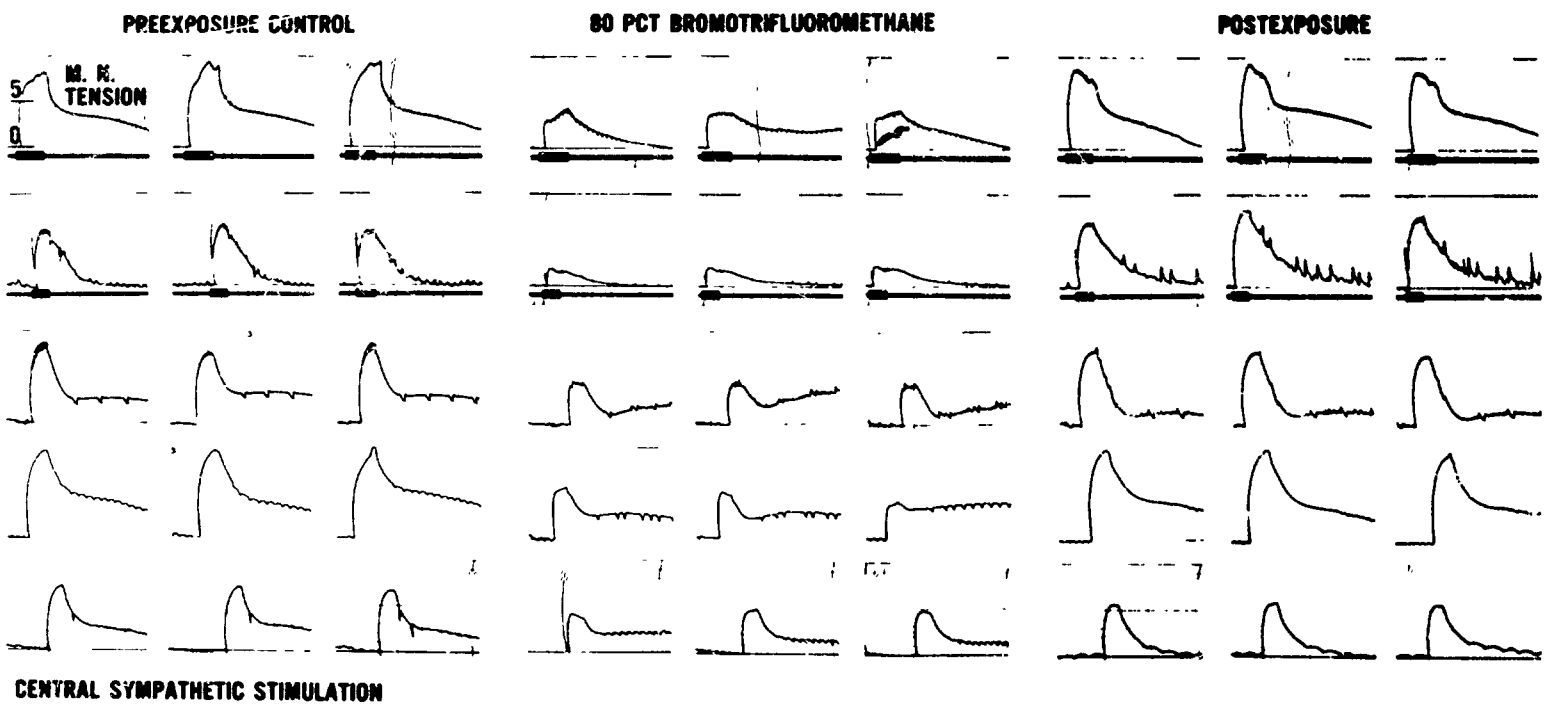


FIGURE 12. Electrical stimuli were applied to the central cut end of the vagosympathetic trunks of five dogs before, during, and after exposure to 80 percent $CBrF_3$. Maximal tension (arbitrary units) developed in the nictitating membrane (M.N.) was significantly lower during $CBrF_3$ exposure.

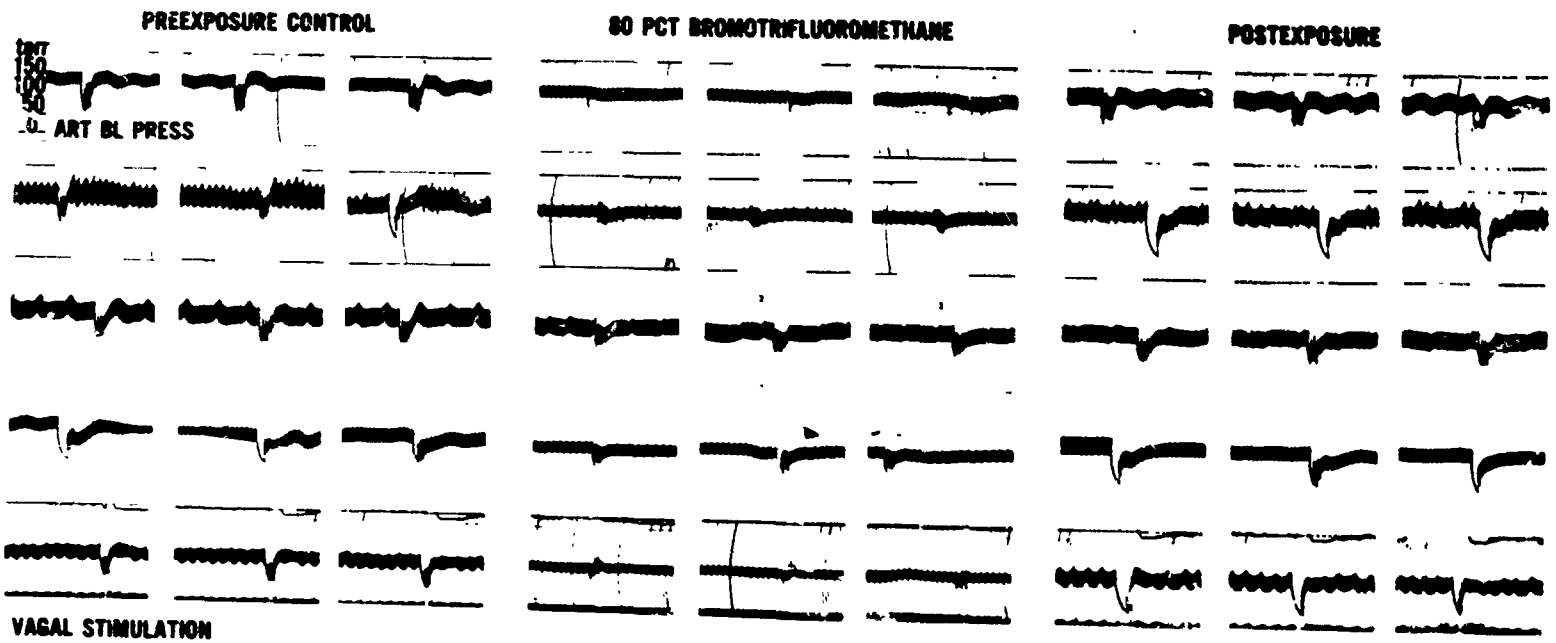


FIGURE 13. Electrical stimuli were applied to the peripheral cut ends of the vagosympathetic trunks of five dogs before, during, and after exposure to 80 percent $CBrF_3$. The degree of vagal inhibition was decreased during the $CBrF_3$ exposure.

involved have been in use in our laboratory for a considerable length of time and are known to be highly reliable. The additional experiments that will complete this study are not expected to alter the conclusions significantly from those expressed here.

Donor and recipient dogs, respectively, were exposed to 15 percent F1211 for five minutes in cross-circulation experiments as described earlier for experiments with F1301. Exposure of the donor resulted in a decrease in the donor mean arterial blood pressure with no change in the cross circulated hind limb perfusion pressure (constant perfusion flow rate). Exposure of the recipient, on the other hand, resulted in a decrease of both the recipient mean arterial blood pressure and hind limb perfusion pressure. These responses to F1211 exposure were unaltered by the pretreatment of both dogs with 0.3 mg/kg atropine sulfate and pretreatment of the donor (and, hence, the recipient perfused hind limb) with two mg/kg of propranolol intravenously. Ten mg/kg of hexamethonium given intravenously to the recipient dog prevented the change in hind limb perfusion pressure during exposure of the recipient to F1211.

These experiments suggest that exposure to F1211 resulted in a decrease in peripheral vascular resistance by causing a decrease in vasoconstrictor tone. F1211 was shown not to have a direct peripheral vascular smooth muscle effect or cause the indirect release of vasoactive humoral agents or local accumulation of vasoactive metabolites. The decreased peripheral vascular resistance was shown not to be the result of the activation of vasodilatory beta-adrenergic or cholinergic receptors peripherally or of active vasodilatation mediated centrally.

A complementary set of experiments has been performed using single, open-chested ten kg dogs. Dogs were exposed to 15 percent F1211 for five minutes, and responses monitored continuously from a period preexposure to 20-25 minutes postexposure. The exposure to F1211 resulted in a reversible decrease in mean arterial pressure. The fall in blood pressure was attributed to a decrease in vasoconstrictor tone and a negative inotropic effect on the heart. The decrease in peripheral vascular resistance was of sufficient magnitude that cardiac output rose during the exposure (8).

In summary, F1301, F2402 and F1211 appear to possess pharmacodynamic actions of the same general kind. The differences appear to be mostly related to the dose necessary to produce the effects on blood pressure, cardiac rhythmicity and the nervous system. Work remains, though, to quantitate the effects of each compound in order to place them in a relative order of potency.

REFERENCES:

1. E. W. Van Stee and K. C. Back, "Short-Term Inhalation Exposure to Bromotrifluoromethane," Toxicol. Appl. Pharmacol. 15:164-174, 1969.

2. E. W. Van Stee and K. C. Back, "Spontaneous Cardiac Arrhythmias Induced by Bromotrifluoromethane," AMRL-TR-68-188, Wright-Patterson AFB, Ohio, 1971.

3. E. W. Van Stee and K. C. Back, "Hypotension During Bromotrifluoromethane Exposure," AMRL-TR-68-182, Wright-Patterson AFB, Ohio, 1971.

4. E. W. Van Stee and K. C. Back, "The Mechanism of the Peripheral Vascular Resistance Change During Exposure of Dogs to Bromotrifluoromethane," AMRL-TR-69-13, Wright-Patterson AFB, Ohio, 1971. Accepted for publication in Toxicol. Appl. Pharmacol.

5. E. W. Van Stee, K. C. Back and R. B. Prynn, "Alteration of the Electroencephalogram During Bromotrifluoromethane Exposure," Toxicol. Appl. Pharmacol. 16:779-785, 1970.

6. P. M. Chikos, E. W. Van Stee and K. C. Back, "Central Nervous System Effects of Bromotrifluoromethane," AMRL-TR-69-130, pp. 81-91, Proceeding of the 5th Annual Conference on Atmospheric Contamination in Confined Spaces, Wright-Patterson AFB, Ohio, 1969.

7. V. L. Carter, Jr., K. C. Back and D. N. Farrer, "The Effect of Bromotrifluoromethane on Operant Behavior in Monkeys," Toxicol. Appl. Pharmacol. 17:648-655, 1970.

8. E. W. Van Stee and K. C. Back, Unpublished data.

DISCUSSION

Dr. Hays: I was not clear, Dr. Back, as to what you are proposing for the cardiac arrhythmia.

Dr. Back: What do you mean, what am I proposing for it?

Dr. Hays: The induction of cardiac arrhythmias following the administration of epinephrine, what does that mean?

Dr. Back: I don't think that epinephrine is necessary to produce it, No. 1, because you can get it without epinephrine. No. 2, although epinephrine certainly causes it, it may not have anything to do with this direct effect on the heart, but rather with a change in pressure, because if I block the heart to the effects of epinephrine with a compound like dibenzoline, and then give epinephrine, which gives you epinephrine reversal in terms of blood pressure effects, you don't precipitate an arrhythmia. So that certainly in order to have an arrhythmia, you must have a blood pressure which is adequate to support it.

Dr. Hays: There have been studies to indicate that pressure is not a factor in cardiac arrhythmia. I wonder if you have looked into the permeability of the muscle, because in the stage of contractility, the

potassium during the depolarization and repolarization is a very important factor in the matter of cardiac arrhythmias. Have you measured potassium exchange?

Dr. Back: No. These experiments are extremely difficult to do, as you well know. No, we have not, and of course I have talked to Peter Dressel about this over the years, who has been working in this area for many, many years. There is a dichotomy here, and I don't know what the answers are. All I can say is that epinephrine is not necessarily needed to cause an arrhythmia, and I don't think you have to administer exogenous epinephrine to cause an arrhythmia. That is proven.

The blockage of certain of the epinephrine effects blocks the arrhythmia, but in the same sense if I then give a blocked animal epinephrine when I increase the blood pressure mechanically, I can cause it. So that blood pressure certainly does have in this instance something to do with arrhythmias.

Dr. Hays: We did some studies some 20 years ago in which we were able to demonstrate that a hypotensive effect of isoprel will produce the same type of cardiac arrhythmia. Therefore we thought that it must have been the positive isotropism that was responsible for the cardiac arrhythmia. Anyone who has worked with cyclopropane has said you do not have to give exogenous epinephrine. If you put any dog on cyclopropane to 20 or 30 percent, you will get cardiac arrhythmia. If you take it back to 16 percent, they are back to normal. You can do this repeatedly. It was our belief that there must be some change in the permeability of the cells during the stage of contractility, and a loss of potassium and a regaining of potassium that is the real basic mechanism, not just one of sensitization. This doesn't really mean anything to me.

Dr. Back: It doesn't to me either. I don't even like the word "sensitization."

Dr. Hays: I don't, either.

Dr. Back: But I do agree with you. We don't know exactly what the absolute mechanism is. We do say that there is a decrease in intrinsic anisotropism of the heart. There is no doubt about it. It is decreased. It is depressed. The contractility is depressed. There is no doubt about it. But we don't know what is going on with potassium flux or calcium flux. We have not tried to block it with EDTA or any of those compounds. There are tons of things to do in this area, and I think people have been working on it for 20 or 30 years now. Dr. Chenoweth worked on it for lo these many years. No one has the absolute answer to this, and of course it is important to Freon 12 and Freon 11. These are the compounds that are very, very potent.

In terms of potency, what are you going to talk about in terms of toxicity? Are you going to talk about the potency of the compound to produce a decrease in blood pressure, or the potency of the compound to cause arrhythmogenic effects? I would caution anybody about the use of the toxicity standards that have been proposed in the past for these compounds. I don't think that the Underwriters' Laboratories dose-effect

chart is of any use whatsoever when you want to assess the use of these compounds, because they mean different things. The LD_{50} is of no consequence whatsoever in this instance. We must reassess the way in which we want to categorize these compounds. Putting 1301 as least toxic is ridiculous; putting 2402 as most toxic is ridiculous, because we are talking about too many different things here. We have got to get away from this old classical idea of how much kills on a volume basis. It is obvious that rats exposed to 30, 40 or 50 percent don't die from any of these compounds. But if you expose a man to any of these compounds at this kind of level, you are going to certainly get death, not because it hurts the liver, but because it may well do something to the heart or the central nervous system or both.

Mr. Wands: I think one of the points that has come out of this discussion is, first of all, that the toxicologists don't have all of the answers clearly agreed upon yet in terms of mechanisms. I think the other thing that is important is the new definition of toxicology that Dr. Back has just brought out. The classical toxicology of number of living and number of dead animals is really meaningless when you are talking about a much different phenomenon, such as the "cardiac sensitization," or cardiac failure perhaps might be a more appropriate term, rather than sensitization, and that we do need new test procedures, and we need desperately to have comparative values by a standard test procedure for a variety of the halogenated fire extinguishing agents, as well as of other materials. We heard mention here of cyclopropane and some of the other anesthetics. It might be pertinent for perspective purposes here to comment that many of the straight hydrocarbon solvents, such as benzine, will also do exactly the same kind of phenomenon. They will create cardiac arrhythmias of one kind or another. So this whole thing needs to be put into a great deal of perspective. Again I do hope that we can approach that perspective during the rest of today and tomorrow in terms of the halogenated fire extinguishing agents.

Mr. Wilson: Dr Back, could you answer whether halogenated agents should be used for extinguishing fires? You said you had some practical ideas and if asked, you might share them. You are asked.

Dr. Back: Yes, they should be used under any and all circumstances as long as one understands what can happen if one is improperly protected. So, yes. None of them should be outlawed because of toxicity, I feel. I feel if they are useful, and they are the best for whatever application you are going to use it for, they should be used fully, realizing that one may have to use a face mask or get out of the room in a big hurry, or he has a certain amount of time in which to use it and he must maybe hold his breath for that length of time, I don't know. But no compound should be outlawed from use because of its toxicity as long as you understand what that toxicity may well entail.

Mr. Wands: I think what Dr. Back has just said is the fundamental principle of industrial hygiene, that there is no material so dangerous but what we cannot find ways and means of working with it properly and safely.

Dr. Fielding: I wanted to ask Dr. Back a question regarding the basic mechanisms at the molecular level of the cardiac and CNS effects. Do you feel these are probably fundamentally the same at the molecular level?

Dr. Back: They may well be. I am really not prepared to say, because we have not done any basic research at the cellular level with three of these compounds. We have done some with dichloromethane, which you heard about before. We have done some with Freon 113, but not enough so that I could say that they are fundamentally the same. I don't think central nervous system tissue reacts the same as heart tissue for the most part. I think the mechanisms are slightly different. I don't know what Dr. Hays would say about this, as a pharmacologist, but I don't think that they are the same exactly. Of course, the ganglionic blocking effect of the compound is slightly different, certainly, than the effect on the contractility of the heart. There is no doubt about that in my mind.

REMARKS

Mr. Wands: Our next speaker this afternoon is Dr. Willard Harris from the University of Illinois Hospital School of Medicine.

CARDIAC EFFECTS OF HALOGENATED HYDROCARBONS

Willard S. Harris

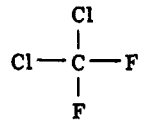
University of Illinois College of Medicine

ABSTRACT

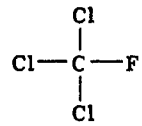
This brief review demonstrates that, contrary to their widespread reputation as inert, the fluoroalkane gases, or Freons, that are used as aerosol propellants are rapidly-acting and potent cardiac toxins. This discovery, first reported in mice, has been confirmed during adequate oxygenation, either in vitro or in vivo, in rats, cats, dogs, monkeys and man. The fluorocarbons, or Freons, that propel aerosols are toxic to the mouse heart, sensitizing it to the early appearance of sinus bradycardia and atrioventricular block during a subsequent partial asphyxic challenge. Our studies have also shown that these gases enter the arterial blood in monkeys, cats and dogs after inhalation and despite adequate oxygenation, rapidly -- by an average of 39 (S.E. $\pm$ 4.2) seconds -- cause ventricular premature beats, ventricular bigeminy, and ventricular tachycardia when breathed by awake or anesthetized monkeys, lower arterial pressure and peripheral resistance in several species, and, a point for emphasis, are directly toxic to ventricular myocardium, quickly and profoundly depressing myocardial contractility in all species (rat, cat, dog, and man) studied. Ventricular tachyarrhythmias, bradyarrhythmias, acute heart failure, arterial hypotension and asphyxia may contribute, singly or in combination, to the sudden death of youths who deliberately inhale aerosol propellants. Our preliminary studies with rat and human papillary muscles suggest that the halogenated fire extinguishing agent, bromotrifluoromethane, or Halon 1301, also directly depresses myocardial contractility.

This presentation, unlike the others, will not be about the halogenated fire extinguishing agents. Instead, I shall discuss a different class of fluorinated hydrocarbons, or Freons, which are not brominated. They are widely used as refrigerants, solvents, and aerosol propellants, but not as fire extinguishing agents. Unlike the fire extinguishants, the aerosol propellants are well-known to cause death in man.

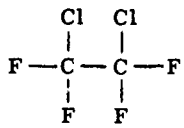
Figure 1 shows the chemical structure of the four most widely used fluorocarbons. The generic name for these materials is "Halon" and there are several relating to specific manufacturers. For convenience, the registered trademark "Freon" of E. I. du Pont de Nemours & Company will be used. Freons 11, 12 and 114 are aerosol propellants, while Freon 113



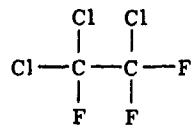
Dichlorodifluoromethane
(Freon 12)



Trichloromonofluoromethane
(Freon 11)



Dichlorotetrafluoroethane
(Freon 114)



Trichlorotrifluoroethane
(Freon 113)

FIGURE 1. Chemical formulae and names of the three most commonly-used aerosol propellants, Freons 12, 11 and 114, and the solvent, Freon 113.

is a solvent. Freon 12 (CCl_2F_2) is the most commonly-used aerosol propropellant. Its boiling point is -21.6°F, and it is a gas at room temperature. Because of its high vapor pressure, it is usually combined, when used to propel aerosols, with Freons 11 or 114 or other propellants, or with solvents. The boiling point of Freon 11 (CCl_3F) is 74.8°F, of Freon 114 ($CClF_2CClF_2$) is 38.4°F, and of Freon 113 (CCl_2FCClF_2) is 117.6°F. Because of its high boiling point, Freon 113 is not an aerosol propellant, but its excellent solvent properties cause it to be widely employed in aerosols.

During the past five years, more than 140 healthy youngsters, usually teen-aged or slightly younger, have died within minutes after breathing for intoxicant purposes, the propellant gases discharged from aerosols. Sudden death and negative postmortem findings suggest that a cardiac mechanism might be responsible for these unexpected deaths.

Possibly of related interest are reports from the United Kingdom (1-3) of an increase, occurring during the middle 1960's in England and Wales, in the incidence of sudden unexpected death among people with asthma. In presenting their epidemiological and clinical evidence, the British investigators have concluded that this excessive mortality was, in the words of Inman and Adelstein (3), "likely to have been the result of over use" of pressurized aerosol bronchodilators, which first became available in the United Kingdom in 1960.

Our experimental results have shown, beyond doubt, that the fluoroalkane propellant gases are directly toxic to the heart and blood vessels. Their cardiovascular toxicity takes several different forms. Certain highlights of our research will be presented briefly in chronological order.

First, a description of the simple and inexpensive way, using mice (4, 5), by which the cardiac toxicity of aerosol propellants was

revealed. In these early studies, done with Mr. George Taylor, who was a fourth-year medical student, mice took three breaths of the fluoroalkane gas (Freons 12, 11 and 114) released by a single discharge of a pressurized bronchodilator nebulizer. Subsequent challenge with partial asphyxia, either immediately or 15 minutes later, was accompanied by the unusually early (i.e., accelerated) appearance of asphyxia-induced sinus bradycardia, atrioventricular block, and ventricular T-wave depression (4).

As defined by previously published results (4), the essence of the technique is to apply a degree of asphyxia that otherwise untreated mice will tolerate for four minutes without developing bradyarrhythmias. Indeed, in mice unexposed to Freon, the degree of partial, or mild, asphyxia applied causes tachycardia, not bradycardia. In striking contrast, after mice inhale three breaths of Freon, which takes about two seconds, application of exactly the same partial asphyxic challenge now causes the early appearance of lethal, asphyxia-induced atrioventricular block and profound sinus bradycardia (defined as a slowing of 200 or more beats/min). It must be emphasized that the asphyxic challenge need not be applied immediately but may be started, for the first time, as late as 15 minutes after the brief exposure to Freon.

Figure 2 summarizes the mean changes of heart rate occurring in three different groups (12, 12 and 18 mice, respectively) of anesthetized (0.5 ml of 0.3% sodium pentobarbital i.p.) mice in a representative study. Partial asphyxia was applied as described previously (4,5). The Freon propellants were administered either with a pressurized bronchodilator nebulizer or as a mixture of 60 percent Freon 12 -- 40 percent Freon 114 supplied by the manufacturer. The sinoatrial heart rate rose throughout four minutes of partial asphyxia in 12 mice previously unexposed to propellant, was unaffected when 12 other mice inhaled propellant in room air for 25 seconds, but slowed an average of 79 beats/min in 18 other mice at 25 seconds of partial asphyxia after only three breaths of propellant. By themselves neither the propellant for 25 seconds nor partial asphyxia for four minutes caused bradyarrhythmias. In contrast, after three breaths of fluoroalkane propellant, the same degree of partial asphyxia caused 2:1 atrioventricular block in 13 of the 18 mice and profound sinus bradycardia in the remaining five. These bradyarrhythmias occurred, on the average, by 35 seconds of asphyxia.

For the technique developed in these early studies to be applied validly, its basic rules must be followed. When the correct degree of partial asphyxia is administered to otherwise untreated mice, no bradyarrhythmias appear for four minutes. If asphyxia of the same intensity is maintained longer, sinoatrial bradycardia and 2:1 atrioventricular block appear by five or more minutes and, eventually, complete heart block and death occur. A brief exposure to the Freon propellants markedly changes the situation, as demonstrated by an earlier, i.e., accelerated, onset of these various bradyarrhythmias when partial asphyxia of the same intensity is subsequently applied. Whereas the application of four minutes of our partial asphyxic challenge evokes no bradyarrhythmias in otherwise untreated mice, pretreatment by three breaths of Freon sensitizes the mice for at least 15 minutes. During this time, application

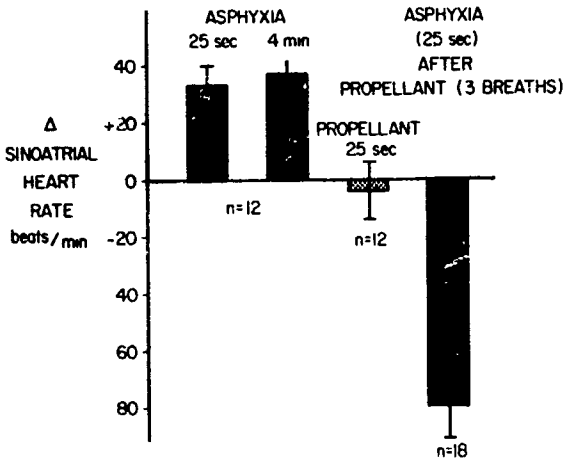


FIGURE 2. Representative study of 42 mice. Application of partial asphyxia caused sinoatrial heart rate to increase at 25 seconds and four minutes of asphyxia in 12 mice. Breathing Freon aerosol propellants in room air for 25 seconds had no effect on heart rate in another 12 mice. In contrast, after a third group of 18 mice had been exposed to only three breaths of the Freon aerosol propellants, application of exactly the same intensity of partial asphyxia now caused marked slowing of sinoatrial heart rate at 25 seconds of asphyxia.

of the same degree of asphyxia now causes 2:1 atrioventricular block or profound sinoatrial bradycardia within a minute or less.

If one decides to study mice with a degree of asphyxic challenge different from that we have described, care must be taken that its intensity is neither too great nor too mild. If the asphyxic challenge is excessive, e.g., if complete asphyxia is applied, otherwise untreated mice will not have tachycardia but, instead, may develop sinoatrial bradycardia and atrioventricular block within a minute or less. As a result, too little time would be left to permit a demonstration that the onset of these asphyxia-induced bradyarrhythmias has been markedly accelerated by previous exposure to Freon. The chance of showing that the Freons are toxic would automatically be abolished by the design of such a "test," which is, therefore, a pseudotest. The results of such a pseudotest would be meaningless, or worse. If the basic fallacy inherent in such a pseudotest were not recognized, false and misleading conclusions might erroneously be drawn. For this reason, the mechanism of this fallacy will be restated briefly in slightly different terms. If asphyxia is made complete, or nearly so, its depressant effect on sinoatrial pacemaking and atrioventricular conducting functions may be too great for an additional depressant effect (additive, synergistic, or sensitizing) of Freon upon these functions to be demonstrated. To modify this test, which clearly and reproducibly shows Freon toxicity to the mouse heart, by using, instead, complete asphyxia, which could not possibly show Freon toxicity, would be wrong. Not only would such a procedure differ irrevocably, but it would not be a "test" for Freon toxicity.

To test the reproducibility of this technique of partial asphyxia, a technician, unseen by the investigators, exposed ten mice at random either to the three consecutive breaths of Freon or to a placebo. As in the original study (4), a mixture of Freons 12, 11 and 114 was released by the single discharge of a pressurized bronchodilator nebulizer. Before inhalation, the mixture was filtered through a cotton gauze placed inside the mouthpiece of the nebulizer. Five mice happened to receive Freon and five received none. One of the investigators (Taylor) then entered the room and applied his usual asphyxic challenge. The 2:1 atrioventricular block or profound sinoatrial bradycardia appeared in less than a minute in each of the five Freon-sensitized mice but did not appear by four minutes of asphyxia in any of the five mice who had not received Freon, each of whom had, in contrast, sinoatrial tachycardia. Thus, the degree of partial asphyxic challenge produced by this technique, which was used in our original study (4), is reproducible enough to differentiate easily the Freon-treated mouse from one not exposed to Freon.

In addition to the studies described in our original report (4), extensive studies have also been done with this technique in more than 200 mice, using in place of the bronchodilator nebulizer, eight different commonly-used household and cosmetic aerosols, an aerosol toy, and pure, commercially-available Freons 12, 11 and 114, singly and in combination. The results have been exactly the same in each instance. It has made no difference whether the asphyxic challenge was applied for the first time immediately after Freon or 15 minutes later. Atropine has failed to block these results, suggesting they are not reflex.

Since sensitization by Freon to the early appearance of asphyxia-induced bradyarrhythmias lasts at least 15 minutes, it cannot be attributed to displacement of pulmonary alveolar oxygen by Freon. The mice take only three breaths of Freon, which would rapidly leave the alveoli both by entering the blood and by exhalation. By 15 minutes, the arterial blood levels of Freons 12, 11 and 114, which are gases at body temperature, would have markedly declined from their peak levels, largely by exhalation but, to a lesser extent, also by entering the tissues. It might be speculated that the fluoroalkane propellant gases may, in "hit and run" fashion, cause residual, but temporary, damage to functional sites somewhere in the murine cardiovascular system, e.g., in the sinoatrial and atrioventricular nodes or elsewhere, or are entrapped or bound there, either unchanged or, perhaps, biotransformed to an active and toxic metabolite. Disappearance of the sensitizing effect of Freon in the mouse, which occurs between 15 and 30 minutes in some of our recent studies, might reflect either repair of its damage or exit of the Freon molecules or their metabolites from the sites of their activity. It must be emphasized that in intact dogs and monkeys, which we have studied, some of the toxic effects of the Freons on the heart disappear much more quickly (e.g., 1-1/2 to 3 minutes) than in mice.

The halogenated fire extinguishing agents have not been tested with the mouse model. It is important to note, however, that the ability of the fluorinated propellants to induce lethal bradyarrhythmias in mice was markedly increased by the subsequent addition of partial asphyxia. These results in mice indicate that exposure to fluorocarbons may be especially hazardous during partial asphyxia. Until the

halogenated fire extinguishants have been fully studied during hypoxemia and partial asphyxia, such as fire produces, the true extent of the toxic danger of the extinguishants will not be known.

The toxic effects of the Freon propellants on the cardiovascular system of the mouse are interesting in their own right and deserve further study. They also have a unique importance in having provided the first demonstration that aerosol propellant gases, previously described as inert, are toxic to the heart. When these first mouse data were published, it was predicted that the fluoroalkane propellant gases would be found toxic to the cardiovascular system in several different ways, dependent, in part, on the species studied (4). Since then, experiments have shown exactly this. These subsequent studies have revealed that the Freons are toxic, in vitro or in vivo, to the cardiovascular system of all five other species that we have studied (rat, cat, dog, monkey and man), despite adequate oxygenation. Moreover, the toxic effects of Freon differ, in many ways, from those of anoxia produced by 100 percent nitrogen.

Fourteen awake or anesthetized monkeys inhaled a mixture of 30 percent Freon 12 - 9 percent Freon 114 - 61 percent O_2 (6). All 14 developed ventricular premature beats, bigeminy, or tachycardia, which began at an average of 39 (S.E. $\pm$ 4.2) seconds. At this time, the concentration of Freons in arterial blood, measured in three monkeys by gas chromatography, averaged 8.2 mg/100 ml. Freon caused the ventricular arrhythmias without lowering arterial oxygen tension or pH or raising arterial carbon dioxide tension and while reducing arterial blood pressure only slightly. For comparison, seven of the monkeys inhaled 100 percent nitrogen without Freon for three minutes, which lowered arterial oxygen tension, on the average, to 30 (S.E. $\pm$ 3.2) mm Hg. Except for one monkey, whose arterial oxygen tension fell to 16 mm Hg, the three minutes of anoxia failed to cause arrhythmias. The ventricular arrhythmias caused by fluoroalkane gases may have been mediated through beta adrenergic receptors, since these arrhythmias were abolished by pretreatment with propranolol, or may have resulted from a nonadrenergic, direct, toxic effect of the gases on the heart. The results, obtained in monkeys breathing the aerosol propellants, Freons 12 and 114, are concordant with the earlier work on the fire extinguishant, bromotrifluoromethane, or Halon 1301, published in 1969 by Van Stee and Back (7), and would suggest that some human deaths after propellant inhalation may be caused by ventricular tachycardia or fibrillation.

The next studies, done with Dr. Signe Kilen (8, 9), have shown that dichlorodifluoromethane, or Freon 12, which is the most commonly-used aerosol propellant gas, directly, rapidly, and profoundly depresses myocardial contractility. Papillary muscles excised from the left ventricles of 29 decapitated rats were studied in a well-oxygenated, constant temperature, muscle bath. The concentration of Freon 12 in the bath fluid immediately next to the muscle was measured by gas chromatography. While aeration of the bath with 99 percent O_2 - 1 percent CO_2 was maintained, Freon 12 gas was bubbled at 43 ml/min into the bath. Developed force was depressed by the third beat after Freon was introduced and rapidly fell further to less than 35 percent of its control

level. When Freon administration was stopped, contractility gradually returned to normal.

Thus, in a group of 14 rat papillary muscles contracting isometrically, developed force and the rate of force development (dF/dt) fell rapidly to 35 percent of control when Freon was given together with O_2 and CO_2. In contrast, substituting nitrogen in place of Freon, while O_2 - CO_2 aeration was continued, had virtually no effect. Without Freon, hypoxia induced by giving 100 percent nitrogen caused less depression than did Freon given together with adequate O_2 and CO_2. Moreover, after 15 minutes hypoxia, the reintroduction of Freon depressed force development much further, almost abolishing it. Since Freon 12 directly depresses myocardial contractility whether the muscle bath is well-oxygenated or deoxygenated, this depressant action cannot be ascribed to hypoxia in the bath medium. On the other hand, when the papillary muscle is exposed to both Freon 12 and hypoxia simultaneously, the myocardial depressant effects of both interventions appear to be additive.

Freon 12 with adequate oxygenation shifted the force-velocity curves downward and to the left more than did hypoxia induced by 100 percent nitrogen, again showing that Freon markedly depresses contractility. Dose-response studies revealed that, in a well-oxygenated bath, Freon 12 clearly depresses myocardial contractility in a linearly dose-related manner. At the highest flow rate, the bath concentration of Freon 12 was the same as found in the arterial blood of anesthetized cats and dogs breathing 25 percent Freon 12 for one to two minutes, while, at the lowest flow rate studied, which depressed developed force 20 percent, the bath concentration of Freon approximated that found in the arterial blood of cats breathing one percent inspired Freon 12 for one minute.

Freon 12 caused a similar depression of contractility in five human left ventricular papillary muscles, which were studied after they had been surgically excised from patients at the time of mitral valve replacement. Freon depressed contractility of the human myocardium in the same linearly dose-related manner as it did in the rat. In the human papillary muscles, 43 ml/min Freon 12 reduced developed force and the rate of force development 50 percent and shifted the force-velocity curves markedly downward and to the left (9).

These results with isolated rat and human papillary muscles are the first demonstration that Freon 12, the most commonly-used aerosol propellant gas, is directly toxic to ventricular myocardium. In a well-oxygenated muscle bath, it directly, quickly, profoundly and reversibly depresses myocardial contractility.

The in vivo effects of Freon 12 inhalation on the left ventricular contractility of anesthetized, closed-chested animals have been determined by Taylor and Harris (9, 10) in cats and by Bielinski, Jain and Harris (11) in dogs. Rapid-speed, high-fidelity recordings of the left ventricular pressure in these animals were obtained through an 18- or 19-gauge needle inserted directly into the left ventricle through

the chest wall. Contractility was assessed by the instantaneous relation of left ventricular dp/dt to developed pressure during the isovolumic phase of contraction. It must be emphasized that Freon 12 had no effect on heart rate in either the pentobarbital-anesthetized cats or dogs.

Without affecting heart rate or rhythm or lowering arterial oxygen tension, the inhalation by 11 cats of a mixture of 25 percent Freon 12 - 75 percent oxygen rapidly raised arterial blood Freon levels and quickly, markedly, and directly reduced the instantaneous relation of left ventricular dp/dt to total and developed pressure throughout the isovolumic phase of contraction and, as a result, depressed the various indices of contractility derived from this relation. In studies of 31 anesthetized, closed-chested dogs, the inhalation of Freon 12 - 21 percent oxygen caused a similar, but somewhat less, depression of myocardial contractility.

Dose-response studies were performed with the cats and dogs inhaling graded inspired concentrations of Freon 12 mixed with adequate oxygen (to yield an inspired concentration of 21 percent oxygen or greater in the cats and 21 percent oxygen in the dogs). Placebo had no effect. In striking contrast, in both the cats and dogs, the arterial blood levels of Freon 12 rose linearly with its inspired concentration, while myocardial contractile state and systolic, diastolic, and mean arterial blood pressures fell rapidly and profoundly in a dose-related manner and total peripheral resistance declined. For example, the highest inspired concentration, 60 percent Freon 12, lowered diastolic arterial pressure of the dogs 40 mm Hg. Autonomic receptor blockade with the combination of atropine, propranolol, and phenoxybenzamine failed to diminish the fall in either aortic pressure or peripheral resistance produced by Freon. The results of these in vivo studies have demonstrated that Freon 12 rapidly enters and leaves the blood and is directly toxic to vascular and cardiac muscle.

Back and associates (7) have clearly shown that inhalation of the halogenated fire extinguishant, bromotrifluoromethane, or Halon 1301, in addition to having other interesting effects, sensitizes the hearts of dogs and monkeys to the induction of ventricular arrhythmias by exogenous epinephrine. More recently, Reinhardt and associates (12) have shown that the aerosol propellants similarly sensitize the hearts of dogs to the ventricular arrhythmic effects of administered epinephrine. It must be emphasized, however, that the fluorinated aerosol propellants are toxic to the cardiovascular system in several other ways as well.

In summary, our studies have shown that the fluoroalkane gases, or Freons, used to propel aerosols sensitize the hearts of mice to the early appearance of asphyxia-induced sinus bradycardia, atrioventricular block and ventricular I-wave depression (4), quickly enter the blood of monkeys (6), cats (9, 10) and dogs (11) after inhalation and, despite adequate oxygenation, have a wide spectrum of cardiovascular toxic effects, for example, directly depressing contractility in rat, cat, dog and human myocardium (8 - 11), lowering arterial blood pressure in the monkey, cat and dog (6, 9 - 11), and rapidly inducing ventricular

arrhythmias in awake or anesthetized monkeys (6). These experimental studies, to date, suggest that ventricular tachyarrhythmias, bradyarrhythmias (sinus bradycardia and arrest and atrioventricular block), acute heart failure, arterial hypotension and asphyxia may contribute, singly or in combination, to the sudden death of persons who deliberately inhale aerosol propellants.

Our studies of the Freon propellant gases lead to three major new conclusions. First, contrary to their widespread reputation as "inert" and harmless (13, 14), the fluoroalkane propellant gases are rapidly-acting and potent cardiovascular toxins. Secondly, they are directly toxic to the myocardium and blood vessels. Thirdly, they are toxic to the heart in not one, but in several different ways.

It must be emphasized, however, that our results were obtained with fluorinated aerosol propellants. A strong enjoiner is made against assuming that all these same results also apply, either qualitatively or quantitatively, to the fluorinated, brominated fire extinguishing agents. On the other hand, unless and until the halogenated fire extinguishants are subjected to at least the same kinds of studies that have been described herein with the aerosol propellants, the cardiac toxicity of the extinguishants cannot be adequately assessed.

In preliminary investigations of isolated left ventricular papillary muscles from five rats and one human, studied in a well-oxygenated muscle bath, Dr. Kilen and Dr. Harris have already found, without exception, that bromotrifluoromethane, or Halon 1301, clearly and directly depresses myocardial contractility. Quantitatively, the Halon 1301 appeared to depress the contractile state of the myocardium in the muscle bath less than the aerosol propellant, Freon 12, did. However, comparison of the two halogenated gases is based on highly preliminary data, and, therefore, this comparison between the two gases (but not the fact that Halon 1301 depresses myocardial contractility) must be considered as only tentative at this time. It is obvious that much more work must be done to test for and define the toxic effects of the halogenated fire extinguishants. In addition, studies are also needed to test the possibility that exposure to asphyxia or to carbon monoxide or the presence of certain diseases, such as coronary artery narrowing, might make some people particularly susceptible to the toxic effects of the halogenated fire extinguishing agents.

REFERENCES:

1. F. E. Speizer, R. Doll and P. Heaf, "Observations on Recent Increase in Mortality from Asthma," Brit. Med. J. 1:335-339, 1968.

2. F. E. Speizer, R. Doll, P. Heaf and L. B. Strang, "Investigation into Use of Drugs Preceding Death from Asthma," Brit. Med. J. 1: 339-342, 1968.

3. W. H. W. Inman and A. M. Adelstein, "Rise and Fall of Asthma Mortality in England and Wales in Relation to Use of Pressurized Aerosols," Lancet 2:279-285, 1969.

4. G. J. Taylor and W. S. Harris, "Cardiac Toxicity of Aerosol Propellants," J. Amer. Med. Ass. 214:81-85, 1970.

5. G. J. Taylor and W. S. Harris, "Glue Sniffing Causes Heart Block in Mice," Science 170:866-868, 1970.

6. G. J. Taylor, W. S. Harris and M. D. Bogdonoff, "Ventricular Arrhythmias Induced in Monkeys by the Inhalation of Aerosol Propellants," J. Clin. Invest. 50:1546-1550, 1971.

7. E. W. Van Stee and K. C. Back, "Short-Term Inhalation Exposure to Bromotrifluoromethane," Toxicol. Appl. Pharmacol. 15:164-174, 1969.

8. W. S. Harris and S. M. Kilen, "Aerosol Propellants Depress Myocardial Contractility," Clin Res. 19:319, 1971.

9. W. S. Harris, S. M. Kilen, G. J. Taylor and S. Levitsky, "Evidence from Animals and Man that Freon Depresses Myocardial Contractility," Circulation 44: Suppl. II, 119, 1971.

10. G. J. Taylor and W. S. Harris, "Depression of Myocardial Contractility in the Intact Mammal by Aerosol Propellant Inhalation," Clin. Res. 19:342, 1971.

11. R. A. Bielinski, W. S. Harris, A. C. Jain and M. M. Abdel-Monem, "Arterial Hypotension and Myocardial Depression Caused by Inhalation of Aerosol Propellant," Circulation 44: Suppl. II, 50, 1971.

12. C. F. Reinhardt, A. Azar, M. E. Maxfield, P. E. Smith, Jr. and L. S. Mullin, "Cardiac Arrhythmias and Aerosol 'Sniffing'," Arch. Environ. Health 22:265-279, 1971.

13. 1971 Physicians' Desk Reference to Pharmaceutical Specialties and Biologicals, (Medical Economics Inc., Oradell, N. J.), 25th Ed., pp. 1082 and 1492, 1970.

14. "Freon," Encyclopaedia Britannica (Encyclopaedia Britannica Inc., Chicago, Ill.), Vol. 9, pp. 924-925, 1971.

DISCUSSION

Mr. Bischoff: Freon 12 has been used as a test gas in the acceptance test of a number of halon 1301 fire extinguishing systems. I would like to have Dr. Harris state his opinion as to the relative risk of this procedure.

Dr. Harris: You will have to pardon me in that I am not quite certain of the question. Perhaps you could express it a little differently.

Mr. Wands: What is the test system?

Mr. Bischoff: Halon 1301 is of the order of magnitude of $5 a pound, and Freon 12 of an order of magnitude of cost of 50 cents a pound. So in order to minimize the cost of an acceptance test, the fire extinguishing concentrations of the agent were in fact achieved in a total flooding situation. Freon 12 was substituted as the test gas for a system designed to discharge Halon 1301. It would seem to me from the information that I have received as very much of a neophyte in this particular area, this seems to be a relatively dangerous procedure in that the toxicity of Freon 12 is substantially greater than 1301, and perhaps should not be a recommended procedure.

Dr. Harris: You mean the Freon 12 is given to humans.

Mr. Bischoff: No, it is used. Let us say you have an area that you are protecting with a fire extinguishing system, and it is designed for 1301. You now want to determine that it is in fact performing as designed, so you run a discharge test. You actually discharge gas into the area. Instead of using the 1301, the expensive agent, you use a less expensive agent, Freon 12. There is a potential of exposure from gas that is leaking from the area, the possibility that the discharge would be premature. There are various conditions that could exist at the time that this test takes place. In your opinion, is it extremely hazardous to use Freon 12 as a test gas? That is my question.

Dr. Harris: I understand now. Again I said that in our little study that we did on the Halon 1301, at least a comparison of it with Freon 12 has to be considered tentative, although it does look pretty good so far as being somewhat less toxic than Freon 12. But I really think we are dealing with two different agents which, while they do share toxicities in common, may have important differences as well, and I personally think, depending on the concentration, that Freon 12 is quite a dangerous compound. So if that is the meat of your question, that would be my answer.

Mr. Wands: I think the key word there may well be concentration. Almost any material is dangerous at high enough concentrations.

Mr. Bendersky: I am confused. Are you saying that the test work for 1301 is not adequate within the standards of 12(a) for use throughout the country according to safety standards? Are you saying that more tests are required based on your Freon experiments? Is that what you are saying?

Dr. Harris: I tried to be extremely meticulous and not go beyond our facts. That is what the terminal comments I gave were addressed to, that we have worked rather meticulously with the aerosol propellants, and I think that somewhat similar work ought to be done with the Halon 1301 and other Halons in order to determine how toxic they actually are, what determines susceptibility to them, and hopefully what the mechanisms are that are causing this toxicity. I had no implications for legal measures.

Mr. Bendersky: I will state the question again. We have listened to a series of lectures which stated that there are toxic effects with and without concentrations of air, of nitrogen, or whatever, a series of tests, and these defined a series of results, which state essentially that people get caught in these rooms, they get out, and they live again essentially within types of concentrations or whatever.

Now, are these essentially adequate to at least define in your mind a level of safety or are tests such as you are talking about necessary before these statements can be judged as true?

Dr. Harris: You will have to forgive me. I am not in the toxicology area, and certainly not in the public health area. I think the decision as to whether the halons are adequately safe to be used under certain situations is certainly not one for me to comment on. But I think to base a decision that they are entirely safe for use under conceivable circumstances would not be a tenable conclusion based upon our findings here. They certainly do affect the heart, as Dr. Back very nicely showed, and as we have concurred. Whether under certain circumstances people with coronary artery narrowing, as I mentioned, might die from it, that is certainly a possibility.

As to whether it should be permitted in certain uses and not in others is certainly not my decision, fortunately.

Dr. Reinhardt: I would like to ask Dr. Harris what concentrations of 1301 he used in showing that it depresses myocardial contractility.

Dr. Harris: I was so grateful to Mr. Wands for inviting me that I did convince Dr. Keeling in the last couple of weeks to do these studies. The concentration is put into the bath at the same rate as the highest dose of Freon 12, and the dose which we compared in the same muscles, which is 43 ml. per minute. As I mentioned, that will give you a concentration in the muscle bath of 11.5 milligrams per 100 ml. of Freon 12, but what the concentration of the Halon 1301 is in the bath, I do not know. That concentration of Freon 12 would be the equivalent of a 25 percent inhaled mixture for one to two minutes by a cat or a dog anesthetized.

Mr. Wands: I think you have seen some extremely preliminary data here that do raise the question, as Dr. Harris has said, that perhaps we need some additional studies of a comparative nature with the halogenated fire extinguishing agents, and that here is another technique that is a feasible laboratory technique for comparing these materials.

Mr. Riley: I would like to ask Dr. Harris to comment on both his own work and also that of Dr. Back. What do you think the effects that you have described would be when you extrapolate your concentration back down to the five to seven percent level that is commonly encountered in hazard analysis in fire protection?

Dr. Harris: It is always safest to stay with one's own data, and not try to extrapolate, which is really what I am trying to do. I really

would not want to extrapolate back, because one would be dealing with a different species and different types of cardiac abnormalities, as I pointed out. I think any extrapolation is what one wishes to say without really having it backed up. To me the problem is much more complicated. It involves the susceptibility of the population that is exposed to the Freon in our case, the Halon 1301 in the case of Dr. Back and his workers. The susceptibility of the population I think really has to be taken into consideration.

One of the reasons I thought it important to come here was not to say that one should not use Halon 1301. Frankly, if I had my choice, I would rather not fry, as Mr. Wands said. But on the other hand, to go wildly forward, as no one has suggested, but to go wildly forward and perhaps employ this in old age homes and hospitals where there might be people in coronary care units or with coronary artery disease unbeknownst to them, then I really think to do this, one really ought to do studies, and they can be done first in experimental animals, in order to determine what the actual risks are. As far as I can tell from the nice studies presented so far, the risks really are not fully known under these circumstances. At least I have not heard them today.

REMARKS

Mr. Wands: Our next speaker is Dr. Douglas Call who is with the Naval Air Development Center, at what used to be known as Johnstown, which has a new mailing address now, but is still just a suburb of Philadelphia. We are very grateful to Dr. Call for being down here with us today to talk to us about the hypobaric effects of these materials.

HUMAN AND RAT EXPOSURES TO HALON 1301 UNDER HYPOBARIC CONDITIONS

Douglas W. Call

Naval Air Development Center

INTRODUCTION

Halon 1301 (bromotrifluoromethane, $CBrF_3$) is a convenient and highly efficient fire extinguishing agent for use on several types of fires (1, 2, 6). This gas is used in portable extinguishers as well as in total flooding systems.

Engine nacelles and cargo compartments of many military and commercial aircraft carry Halon 1301 fire suppressing systems. Similar systems have been proposed for protecting the occupants and contents of aircraft cabins and flight decks.

Several studies, conducted at normobaric conditions, indicate that laboratory animals and humans can be exposed briefly to Halon 1301 concentrations necessary to extinguish fires in enclosed spaces without developing the central nervous system or cardiac effects that sometimes attend inhaling low levels of other halogenated hydrocarbons (2, 3, 4, 11). However, little information is available concerning the toxicity of Halon 1301 at reduced atmospheric pressures, such as would accompany its use in flight.

To test possible potentiating effects of hypobaric conditions and the resulting hypoxia on any physiologic alterations produced by Halon 1301 inhalation, the following investigation was conducted.

METHODS AND MATERIALS

Rat Studies:

Seventy-two ad-libitum fed, male, Charles River rats weighing 450-550 grams were divided into four groups. Individual animals in each group were exposed to one of the following four conditions:

1. simulated altitude with added Halon 1301 (27 rats);
2. simulated altitude without Halon 1301 (9 rats);
3. simulated altitude with added Halon 1301 and injected epinephrine (27 rats); and

4. simulated altitude without Halon 1301 but with injected epinephrine (9 rats).

Each rat was lightly anesthetized with amobarbital (50 mg./Kg., I.P.), prepared for continuous electrocardiographic recording (lead II), then placed in a small hypobaric chamber. The chamber door was secured and the desired barometric pressure -- 760 mm.Hg. (sea level), 632 mm. Hg. (5,000 ft.), or 380 mm.Hg. (18,000 ft.) -- was obtained.

After the rat had been at these conditions for three minutes, pre-measured amounts of Halon 1301 to produce concentrations of approximately 8, 16, or 24 percent by volume were added directly into the top of the chamber. A metal baffle placed over the inlets served to disperse the incoming gas throughout the enclosure. The final Halon 1301 concentration was measured by gas chromatography.

In each control exposure (Groups 2 and 4), a pulse of compressed air which produced similar noise and pressure changes was added in place of the $CBrF_3$.

After a five-minute exposure to the experimental gas, the rat was returned to ambient conditions. Two-thirds of these animals were then sacrificed immediately by a blow on the head and sections of their lungs were excised and fixed in 10 percent N-buffered formalin and prepared for histologic study. The remaining rats were observed daily for one month.

The rats in Groups 3 and 4 were treated the same as all others except that they received an intramuscular I.M. dose of ten μg./Kg. epinephrine just before they were placed in the hypobaric chamber.

Electrocardiographic records were made at frequent intervals on all rats during each exposure.

Human Exposures:

Eight active-duty military personnel (ages 20-35 years) were exposed for three minutes to either four or seven percent Halon 1301 in air in a hypobaric chamber maintained at 760 mm.Hg., 632 mm.Hg., or 380 mm.Hg. In control exposures, compressed air was admitted to the chamber environment in place of Halon 1301. The gaseous composition of the chamber was monitored by gas chromatography.

Before, during, and after exposure to the experimental gas, each volunteer performed a battery of psychomotor tests which included complex reaction time measures and a finger-maze tracking task. Each subject had 20 training sessions on the psychomotor tasks over a two-week period prior to the experiment.

Electrocardiographs (lead II) were obtained on each subject at regular intervals during all exposures. Physical examinations and pulmonary function measurements were performed on all subjects before and after each exposure.

This was a single blind experiment in that the subject was not aware of which experimental gas was inhaled.

RESULTS

Rat Studies:

No rats died during any chamber exposure. Three animals developed cardiac arrhythmias during inhalation of Halon 1301. One rat breathing 24 percent Halon 1301 at a simulated altitude of 5,000 ft., and one exposed to 16 percent $CBrF_3$ at 380 mm.Hg., developed premature atrial contractions about one minute after the Halon 1301 was admitted to the chamber. Indications of bundle branch blocks appeared as the exposure continued. In both cases, these changes disappeared when the $CBrF_3$-air mixture was replaced with room air during the chamber descents.

Premature atrial contractions were also noted in the electrocardiogram of one rat breathing 24 percent Halon 1301 at 632 mm.Hg. This animal had received an epinephrine injection before the exposure. Normal ECG tracings reappeared when the rat was returned to ambient conditions.

No other prolonged cardiac arrhythmias were noted on the electrocardiograms from any other rats.

None of the animals saved for the one month post-exposure observation died during that period.

Histological examination of the lungs from rats sacrificed immediately after exposure showed no pathologic changes which could be directly related to breathing Halon 1301 or exposure to hypobaric conditions.

Human Exposures:

All post-exposure physical examination results and pulmonary function measurements were similar to pre-exposure values.

Subjects' electrocardiograms obtained during the chamber exposures showed only non-specific changes from control tracings. No alterations were noted that could be directly attributed to the Halon 1301 exposure or to the simulated altitude attained.

Complex reaction time test: An analysis of variance showed statistically significant increases in complex reaction time with Halon 1301 exposure $F(2,28) = 7.39$; $p<0.01$. No other effects were observed.

Maze tracking task: Analyses of variance were performed on the following measures: (1) total time; (2) number of errors; (3) time in error; and (4) average time per error. Inhalation of Halon 1301 produced no significant changes in any of these measures. However, the number of errors on the maze tracking task was found to be significantly influenced by exposure to simulated altitude $F(2,28) = 3.72$; $p<0.05$.

Six of the eight subjects noted subjective symptoms of dizziness, faintness, or drowsiness during exposure to seven percent $CBrF_3$. These symptoms occurred with nearly equal frequencies at each simulated altitude. Three subjects reported these symptoms during each exposure to seven percent Halon 1301.

Similar subjective descriptions were given by three subjects while inhaling four percent $CBrF_3$. These symptoms were reported once at each of the three chamber pressures.

Two subjects experienced the above symptoms during control exposures at 380 mm.Hg.

It was not possible to directly correlate the incidence of subjective symptoms during exposure to the experimental gases to psychomotor performance evaluations.

DISCUSSION

Rat Studies:

Halon 1301 is a member of a large family of halogenated hydrocarbons that are known to induce cardiac arrhythmias when inhaled during times of elevated blood epinephrine levels. These changes often originate in the ventricular myocardium and can produce sudden death. Several investigators have studied this effect in both animals and humans (2, 5, 9, 10, 11).

The cardiac arrhythmias noted in the three rats in the present study were not as serious, nor did they appear as frequently, as those reported by the Haskell Laboratory (2) for a group of dogs breathing similar concentrations of $CBrF_3$ at sea level. However, all of these dogs received an intravenous injection of 8-10 mg./Kg. epinephrine during the exposure to Halon 1301. No abnormal heart rhythms were observed in animals that did not receive exogenous epinephrine. Van Stee and Back (11) demonstrated that dogs and monkeys exposed to 10-80 percent $CBrF_3$ developed spontaneous cardiac arrhythmias at different rates and to different degrees. These two species also exhibited contrasting central nervous system responses to the gas. Earlier, Paulet (8) had established that rabbits, mice, guinea pigs, and rats vary in their susceptibilities to the toxic effects of Halon 1301. Therefore, it is not possible to directly compare the myocardial response of the rats in this study to those observed on other laboratory animals breathing similar Halon 1301 air mixtures.

The low incidence of discernable electrocardiogram changes, and the nature of these arrythmias, indicate that under the conditions studied Halon 1301 is not a very potent cardiac sensitizing agent in rats.

The lack of any pathologic pulmonary changes directly attributable to exposing rats in this study to Halon 1301 at simulated altitude, corroborates the results of another investigation. MacFarland (6)

exposed several laboratory species, including rats, to 10, 15 and 20 percent $CBrF_3$ for two hours at sea level. Lungs, livers, and kidneys taken from some animals immediately after, and from others on the 7th and 14th day post-exposure, revealed no significant changes from control tissues.

Inhaling Halon 1301 at reduced atmospheric pressure does not seem to be any more harmful to laboratory rats than similar exposures at ambient conditions.

Human Exposures:

Two other laboratories have performed human exposures to Halon 1301, both at sea level conditions (5, 10). Reinhardt and Stopps (10) noted no disturbances in cardiac rhythm in three subjects exposed for 3.5 minutes to 1, 3, 5, 7 or 10 percent Halon 1301. At the Hine Laboratory (5), volunteers breathed five or ten percent Halon 1301 in air for up to 20 minutes with no serious cardiac effects. One subject did, however, develop a spontaneous cardiac arrhythmia after inhaling 14 percent Halon 1301 for five minutes. This condition resolved within two minutes after the inhalation was discontinued.

Since no cardiac rhythm changes were noted in the present study that could be directly attributable to Halon 1301 exposure, simulated altitude, or their interaction, it appears that human cardiac response to inhaling this gas at hypobaric conditions is not different from similar exposure at sea level.

Central nervous systems depression is another effect of Halon 1301 inhalation that has been extensively investigated in both laboratory animals and humans (2, 5, 10, 11, 12). In the two sea level human studies (5, 10), volunteers demonstrated a general trend towards loss of muscular coordination and alertness as the $CBrF_3$ percentages in their breathing mixtures were increased. These impairments in mental and physical skills began to appear at Halon 1301 concentrations of five to seven percent. No statistical analyses of the performance data were presented in either report, so it is not possible to directly compare the magnitude of the changes to those observed on similar tests in the present investigation.

The significant increases in complex reaction time during Halon 1301 inhalation noted in this study seem to agree with the usual effect of the gas. However, the subjects' performances on the maze tracking task were not significantly affected by exposure to Halon 1301. Since different neuromuscular skills are necessary to perform different psychomotor tasks, it is to be expected that these skills could be affected to different degrees by exposure to the same agent. This type of response was demonstrated by the subjects in Hine's experiment (5) while they were inhaling five percent $CBrF_3$ in air.

The subjective symptoms described by six of the eight subjects in the present survey were similar to those described by the subjects in the reports discussed above (5, 10). These effects were independent of altitude and thus would seem to be related to the Halon 1301 rather than to altitude hypoxia. At no time was any subject affected to such a

degree by this gas that he was unable to do assigned tasks. These symptoms subsided rapidly after oxygen masks were used. Romberg and self-balancing tests administered to the subjects immediately after leaving the chamber indicated no residual upsets in balance.

The effects of hypoxia on human psychomotor performance are variable and not always directly related to decreasing oxygen partial pressures in the breathing mixtures. Also, some performance tests are more sensitive to the effects of hypoxia than others (4). Therefore, it is not surprising that, during exposure to simulated altitude, subjects in this study made significantly more errors on the maze tracking task than they did at ambient conditions, but no altitude-related performance changes were noted in the other measures.

CONCLUSIONS

This investigation has extended human exposure to Halon 1301 to the concentrations and barometric pressures which might attend its use in a total flooding system in flight. There does not seem to be a significant interaction between hypobaric conditions and the resulting hypoxia and Halon 1301 inhalation on the cardiac or central nervous system effects measured in this study.

Therefore, the presently accepted National Fire Protection Association standard on Halon 1301 total flooding systems for normally occupied spaces (7) may be applicable for aircraft cockpit and cabin installations. However, in all such systems the transient concentration gradient which develops whenever the fire suppressing agent is admitted to the enclosure must be considered. Even though no serious effects seem to accompany breathing seven percent $CBrF_3$ for three minutes at a simulated cabin altitude of 18,000 feet, there is presently no way to predict if persons seated close to the system outlets could safely tolerate the high agent concentrations which would be briefly present until the gas was thoroughly mixed with cabin air. Perhaps an alarm system is necessary to allow passengers time to put on oxygen masks before the gas is released.

At any rate, the convenience and effectiveness of Halon 1301 as a fire extinguishing agent demand that work continue to find ways to take full advantage of this agent's potential usefulness.

REFERENCES:

1. Anon., "du Pont 'FREON' FE1301 Fire Extinguishing Agent," Report B-29B, E. I. du Pont de Nemours & Company, Wilmington, Del., 1969.

2. Anon., "Toxicology of du Pont FE1301 Fire Extinguishing Agent," Report S-35A, E. I. du Pont de Nemours & Company, Wilmington, Del., 1971.

3. W. J. Clayton, Jr., "Fluorocarbon Toxicity and Biological Action," Fluorine Chem. Rev. 1:197-252, 1967.

4. U. Fiorica, M. J. Burr and R. Moses, "Effects of Low-Grade Hypoxia on Performance in a Vigilance Situation," Aerospace Med. 42:1049-1055, 1971.

5. C. H. Hine, H. W. Elliott, J. W. Kaufman, S. Leung and M. D. Harrah, "Clinical Toxicologic Studies on 'FREON' FE1301," Paper No. 11, In: Proc. 4th Ann. Conf. Atmos. Contam. in Confined Spaces, AMRL TR 68-175, Aerospace Med. Res. Lab., WPAFB, Ohio, pp. 127-142, Dec., 1968.

6. H. N. MacFarland, "Acute Inhalation Exposure - Monkeys, Rabbits, Guinea Pigs and Rats - 'FREON' FE1301," Final Report, Hazleton Laboratories, Inc., Falls Church, Va., Nov. 7, 1967.

7. National Fire Protection Association, "Halogenated Fire Extinguishing Agent Systems (Halon 1301), 1971," NFPA 12A, 1971.

8. G. Paulet, "Etude Toxicologique et Physiopatholoque du Monobromotrifluoromethane ($CBrF_3$). Arch. Mal. Prof. 23:341-348, 1962.

9. C. F. Reinhardt, A. Azar, M. E. Maxfield, P. E. Smith, Jr. and L. S. Mullin, "Cardiac Arrhythmias and Aerosol 'Sniffing'," Arch. Environ. Health 22:265-279, 1971.

10. C. F. Reinhardt and G. J. Stopps, "Human Exposures to Bromotrifluoromethane," Report No. 230-66, Haskell Laboratory for Toxicology and Industrial Medicine, E. I. du Pont de Nemours & Company, Wilmington, Del., Dec. 1, 1966.

11. E. W. Van Stee and K. C. Back, "Short-Term Inhalation Exposure to Bromotrifluoromethane," Toxicol. Appl. Pharmacol 15:164-174, 1969.

12. E. W. Van Stee, K. C. Back and C. B. Prynn, "Alteration of the Electroencephalogram During Bromotrifluoromethane Exposure," Toxicol. Appl. Pharmacol. 16:779-785, 1970.

DISCUSSION

Mr. Hanbury: I have two questions. One is it seems to me an earlier speaker said that actually because of the heart arrhythmia condition, dogs should be used rather than mice and so forth as test animals.

The other is are you advocating this halon in a closed system, a closed environmental system like you have in an aircraft, at a certain altitude, or have you ways to expel this gas?

Dr. Call: In answer to the first part, I think that was Dr. Clark that was talking about the laboratory animal to use. As Dr. Back mentioned earlier, sometimes you use what you have. This is how we started with the rats.

In answer to the second question, whenever you have a vehicle away from the earth, you have somewhat of a closed environment. You can't always dump out material very rapidly. The aircraft this was specifically designed for, the E-2, is a pressurized aircraft, and also there is a system within the aircraft, a ventilation system which cycles the air around and cools the instruments, which generate a lot of heat. So there is somewhat of a problem there, after this was dumped off, of remaining around for a while until the pressurization was dumped, and you got a complete fresh supply of air in there. I think we will hear papers tomorrow from some people from FAA in relation to actual applications in civilian cargo and personnel spaces.

I don't know if this really answers your question.

Mr. Hanbury: That was a personnel space, too, that you were talking about.

Dr. Call: Yes, sir, it definitely is. This is a five-passenger aircraft, and the areas where this gas is dumped out are definitely right next to where these people are sitting.

Mr. Hanbury: And you made reference to the NFPA which cautions people against using this agent where you cannot evacuate or get the people out.

Dr. Call: That is the reason for your question. In this case, this aircraft does have the unique fire hazard, and we are trying to protect against it. The pressurization system is such that you can get a rather rapid turnover of the air in there once the fire is out.

Mr. Wands: Perhaps the question relates to the time of exposure.

Dr. Call: I don't know if I said that. I think maybe I did not. Our exposures were for three minutes.

Mr. Phillips: I believe you did mention earlier in your talk, and I would like to make sure it is repeated, that in another exposure condition you had 100 percent fatalities. That was in a fire?

Dr. Call: No, this was the loss of an aircraft due to a fire.

Mr. Phillips: I expect that we will perhaps have a little bit better exposure if we use some agent to put that fire out.

Dr. Call: Yes, sir, that is exactly right.

Mr. Phillips: If we do not put the fire out, we may accept that same type of responsibility we had before, total loss.

REMARKS

Mr. Wands: I am personally very pleased to see the concerns of this audience for maintaining human life and avoiding frying. I sympathize with this 100 percent as a potential victim some day. Certainly this is our prime concern here. We are struggling to find ways and means whereby these materials can be made most effective for that ultimate goal.

Our next speaker this afternoon is Dr. Travis Griffin from the Albany Medical College of Union University. He is going to talk to us about some of their studies on toxicological responses to a variety of halogenated hydrocarbons.

TOXICOLOGICAL RESPONSES TO HALOGENATED HYDROCARBONS

Travis B. Griffin, James L. Byard and Frederick Coulston

Albany Medical College of Union University

Halogenated hydrocarbons are widely used in industry with the fluorinated methanes and ethanes having found important uses as dielectrics, refrigerants, propellants, organic solvents and fire extinguishers and suppressants. These compounds (termed fluorocarbons since the properties are largely governed by the fluorine moiety) are commanding an increasing market in consumer products such as food toppings, hair sprays, deodorants, etc., from their use as propellants. Although the interest of this laboratory in fluorocarbons is broadbased, attention has largely been addressed to the study of candidate fire extinguishers and fire suppressants. The list of compounds investigated incorporates 11 different halogenated hydrocarbons, including the anesthetic halothane (Table 1), but most attention has been directed to studies of bromotrifluoromethane (Halon 1301) and hexafluoroethane (Freon 116). Some detailed attention has also been given to 1,2-dibromotetrafluoroethane (Halon 2402), dichlorodifluoroethane (Freon 12) and octafluorocyclobutane (Freon C-318).

Exposure of animals by the route of inhalation is important since the compounds are either gasses or highly volatile liquids at ambient temperatures and pressure. This route of administration was chosen for the majority of the studies. The investigations have involved the use of three different types of inhalation exposure in laboratory animals. In the first, animals have been exposed for a single short period of time (a few minutes up to one hour) and the immediate effects of exposure assessed. Exposures of this type have been widely used in studies of effects on biochemical systems, pharmacologic effects and studies of metabolism and tissue distribution of the compounds. The results obtained in the single short-term exposures will be emphasized in this presentation. Other investigations have employed the use of multiple intermittent exposures and currently studies are being conducted in which animals are exposed continuously for periods up to 23 hours per day or longer in environmentally-controlled exposure chambers.

In deciding on the type of exposure to be employed in a given experiment it was considered how humans would be exposed as a result of the intended use of the halocarbon. Bromine-containing fluorocarbons, such as Halon 1301, are good fire extinguishers and have been studied from the standpoint that they will be used in situations resulting in brief exposures of humans. They have not received extensive study in continuous exposure situations. However, if such a compound were used in an enclosed atmosphere such as that of a spacecraft, it could remain as part of the atmosphere for an extended period and occupants of the

TABLE 1

Compounds of Interest

A. Substituted Methanes

Halon 1301	Bromotrifluoromethane	$CBrF_3$
Halon 1202	Dibromodifluoromethane	CBr_2F_2
Freon 11	Trichlorofluoromethane	CCl_3F
Freon 12	Dichlorodifluoromethane	CCl_2F_2

B. Substituted Ethanes

Freon 116	Hexafluoroethane	CF_3-CF_3
Freon 115	Chloropentafluoroethane	$CClF_3$-CF_2
Freon 114	1,2-Dichlorotetrafluoroethane	$CClF_2$-$CClF_2$
Halon 2402	1,2-Dibromotetrafluoroethane	$CBrF_2$-$CBrF_2$
Freon 113	1,1,2-Trichloro-1,2,2-trifluoroethane	CCl_2F-$CClF_2$
Halothane	Bromochlorotrifluoroethane	CHBrCl-Cf_3

C. Other

Freon C-318	Octafluorocyclobutane	C_4F_8

vehicle would be in a continuous exposure situation. On the other hand, compounds such as Freon 116, which have been proposed for use as fire suppressants, might deliberately be incorporated into the spacecraft atmosphere resulting in continuous exposure of human beings.

With regard to immediate toxic effects as judged by behavioral responses of laboratory animals during exposure, the present studies have shown that animals appeared to tolerate well single as well as multiple exposures to Halon 1301, Freon 116 and Freon C-318. Halon 1301 and Freon 116 are both well-tolerated by rats and guinea pigs at atmospheric concentration as high as 20 percent. Higher concentrations of these compounds have not been studied in intact, unanesthetized animals. By contrast, laboratory animals are less able to tolerate exposures to five percent concentrations of Halon 1202, Halon 2402, or Freon 113. All three of these compounds caused convulsive movement in rabbits, and Halon 1202 caused violent convulsions and death in rats. These observations are in accordance with the generally-accepted principle relating the chemical constitution with the toxicity of many of the fluoroalkanes, namely a lower toxicity is associated with an increasing number of fluorine atoms in the molecule (Clayton, 1966). The low order

of toxicity in highly fluorinated alkanes is a reflection of low-chemical reactivity and low-biological activity. Since one of the goals of this research is to select at least one compound suitable for controlled, continuous exposure in human volunteers, the more detailed investigations have centered largely around less toxic compounds.

One biological action of halocarbons which is well recognized is the phenomenon of sensitization of the myocardium to epinephrine. Studies of these effects are extremely important and are covered in greater detail elsewhere in this symposium. Suffice it to say that studies of cardiac sensitization are included in our general investigations on fluorocarbon toxicity and that the results are consistent with the findings of others in this area. Compounds containing chlorine, such as the Freons 11 and 12, are among the most potent sensitizers investigated while the perfluorinated compounds, for example Freon 116, are among the least active cardiac sensitizers.

Because of the non-polar character and subsequent high degree of lipid solubility of the compounds under investigation, it is conceivable that they may exert effects on biological lipid membrane systems. In an investigation of this possibility, some of our studies were directed to the effects on mitochondrial function in tissues obtained from animals exposed to fluorocarbons. Some of the early investigations suggested that exposure of rats to halogenated hydrocarbons may have some effect on respiration and oxidative phosphorylation in isolated mitochondria. However, more thorough investigations failed to substantiate any such effects. The results of studies of effects on oxygen consumption are shown in Figure 1. In these studies, mitochondrial functions were measured in animals which were sacrificed immediately following a single exposure to the halocarbon under the conditions shown in the Figure. It can be seen that, in general, the levels of oxygen consumption in mitochondria from the exposed animals were within the range of control values obtained for each of the five tissues studied. A similar pattern of response was seen for oxidative phosphorylation shown in Figure 2. There is, however, a suggestion of enhanced mitochondrial function, e.g., phosphorylation in mitochondria from brain of animals exposed to Halon 1301, Freon 116 or Freon C-318. The effect, if real, more likely means that the compounds may have protected the mitochondria from uncoupling during isolation. Further investigation would be required to substantiate this observation.

Preparation of mitochondria for assay of enzyme activities requires homogenization and centrifugation techniques. These treatments certainly reduce, if not entirely eliminate, the content of gaseous halocarbons in these preparations. In an attempt to overcome these difficulties, an experiment was designed to expose isolated mitochondria *in vitro* to the halocarbons. In order to accomplish this, the isolated mitochondria were placed in the respirometer, but the air in the respirometer was replaced with air containing 20 percent by volume of either Freon 12 or Halon 1301. Oxygen consumption was then measured with the instrument as usual, but during the actual exposure to the halocarbons. Studies carried out with liver and heart mitochondria did not demonstrate any changes in oxidation or phosphorylation.

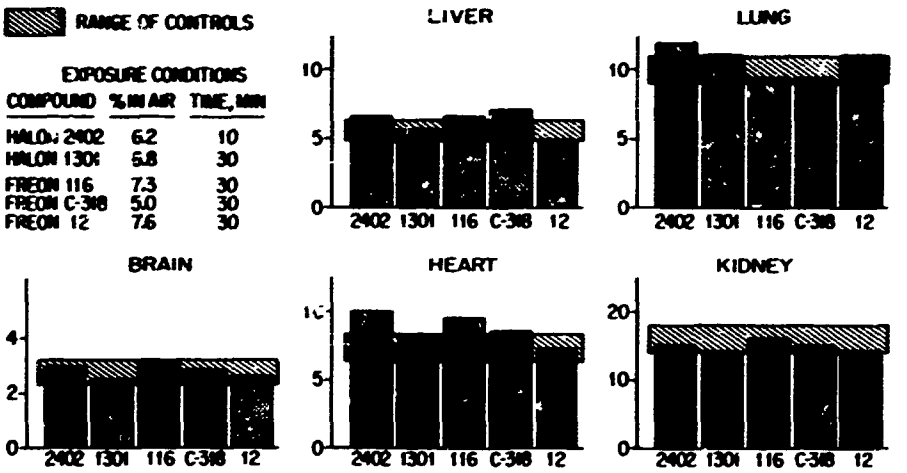


FIGURE 1. Oxygen consumption in mitochondria from rats exposed to halocarbons. Mitochondria were isolated from tissues after the rats were exposed under the indicated conditions. Mitochondria from controls were assayed simultaneously with the experimental groups and the range of activities includes data from all five groups of controls. The rate of oxygen consumption is expressed as mμAO consumed/mg protein /min X 10^{-1}.

Mitochondrial function in animals exposed continuously to fluorocarbons has also been examined. An experiment involving exposure of rats continuously to an average of 5.3 percent Halon 1301 for one month (vide infra) also failed to demonstrate any decrement in mitochondrial function in heart, lung, brain, kidney or liver.

Although the efforts to date have not revealed strong interactions between halocarbons and oxidative enzyme systems of mitochondria, work by others has demonstrated the formation of a cytochrome P-450 substrate complex with perfluoro-n-hexane (Ullrich and Diehl, 1971). The system used was a rat liver microsomal preparation. It was shown that perfluoro-n-hexane in contrast to n-hexane was not hydroxylated by the microsomal monooxygenase system but that the fluorocarbon formed an enzyme-substrate complex and stimulated NADPH oxidation. Hydrogen peroxide was not formed and it was concluded that the fluorocarbon acted as a typical dead-end inhibitor of the microsomal monooxygenase system and led to the uncoupling of electron transport from monooxygenation.

Any biological response to a fluorocarbon, whether it be sensitization of the myocardium or any other manifestation of effect, requires transport of the agent to the primary site of action. Assessment of this can be made through measurement of tissue levels. In the first such experiments, attempts were made to measure concentrations of the halocarbons in the tissues of animals immediately following exposure to the compounds. The results of such a study in which rats were exposed to Halon 2402 are shown in Table 2. In this experiment, the rats were exposed to 3.7 percent vapor concentration of Halon 2402 for 30 minutes. Immediately following the exposure, and at intervals thereafter, pairs

OXIDATIVE PHOSPHORYLATION IN MITOCHONDRIA FROM RATS EXPOSED TO HALOCARBONS

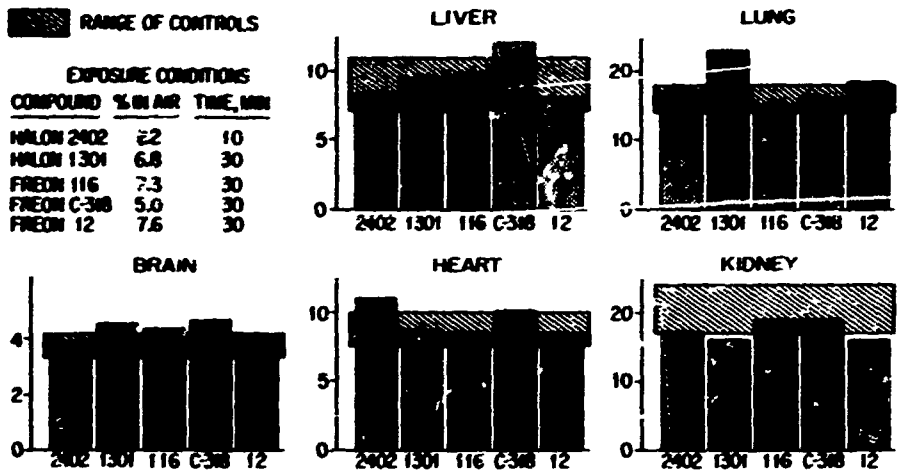


FIGURE 2. Oxidative phosphorylation in mitochondria from rats exposed to halocarbon. Mitochondria were isolated from tissues after the rats were exposed under the indicated conditions. Mitochondria from controls were assayed simultaneously with the experimental groups and the range of activities included data from all five groups of controls. The rate of phosphorylation is expressed as mμ Moles P_i esterified/mg protein/min X 10^{-1}.

TABLE 2

Levels of Halon 2402 in Rat Tissue Following Exposure by Inhalation

Tissue	Post-Inhalation Interval (Hrs) 0	1-1/2	2	24
Liver	258[a]	5	2	0.28
Lung	44	18	2	0.18
Brain	0.70	2.1	0.78	0.36
Kidney	82	27	23	0.33
Heart	24	2.1	2	1.1
Muscle	73	19	2.8	1.0
Fat	365	469	410	11
Blood	87	7	0.23	0.22

a All values shown are in g Halon 2402/g tissue.

of rats were sacrificed and tissue levels of Halon 2402 measured. Detectable concentrations of the compound were present in the animal even 24 hours after exposure. The increase of concentration of Halon 2402 in brain tissue and fat tissue demonstrates that the 30-minute exposure to the compound was not long enough to establish an equilibrium in the animals. The half-life of the compound in blood was less than one hour.

One interesting aspect of this study concerned the relationship, or lack thereof, between levels of Halon 2402 in the brain and the CNS effects as evidenced by behavior. Although behavior patterns returned to normal within 15 minutes after cessation of exposure, brain levels were apparently higher 1.5 hours after exposure and were significantly elevated even three hours after exposure.

Since blood is a readily accessible tissue, and may be obtained without sacrificing the animal, additional studies were made in blood to compare the absolute amount of halocarbon following exposure and the half-life in blood. The results of such a study with Halon 1301 are shown in Table 3. In this investigation, anesthetized rats were placed in the chamber and exposed to a vapor concentration of five percent Halon 1301 for 30 minutes. Levels of Halon 1301 were then determined in blood obtained by heart puncture. These data show that the half-life of Halon 1301 is much less than the 30 minutes observed for Halon 2402. Accurate assessment of half-life from these data is not possible since the 0-time was actually a period 0.5 minutes to 1.5 minutes following removal of the animals from exposure since this amount of time was required to obtain the blood samples.

TABLE 3

Halon 1301 in Rat Blood Following a Single 50-Minute Exposure to a Vapor Concentration of 5% (V/V)

Post-Inhalation Time (Hrs)	Blood Level µg/g
0	5.6
0.25	0.62
1.0	0.35
2.0	0.05
4.0	0.07

It should be noted at this time that in order to obtain any meaningful results at all with a gaseous halocarbon, it was necessary to

utilize methods representing a significant departure from usual procedures. Whereas with the liquids, such as Halon 2402, solvent extraction techniques provided quantitative results, severe losses were observed when the techniques were applied to the gaseous halocarbons. In order to obtain quantitative data with the gaseous compounds, it was necessary to employ techniques involving head-space analysis. In these procedures, blood was withdrawn from the animals by techniques which did not allow the blood samples to come in contact with air. The sample was then transferred quantitatively to a small vial which was sealed with a septum. After a suitable period to allow equilibrium conditions to be obtained within the vial, the gaseous halocarbon was quantitatively determined in the air space within the vial itself.

Previously animals were withdrawn from exposure chamber, sacrificed, and blood was removed for analysis. In these studies with Halon 1301, using the improved head-space analysis technique, it soon became evident that more suitable approaches would be required in making meaningful estimations of blood levels of low boiling materials during the exposure of the animals. The data indicated that very rapid decreases in blood concentrations occurred during the first few minutes after cessation of exposure. The time required to obtain the blood sample after the animal was removed from the chamber was long enough, in relation to the half-life of the gasses in blood, to preclude accurate estimation of blood levels during exposure. In order to overcome these difficulties, a different type of procedure was followed.

For these studies, Dutch-belted rabbits were chosen as the experimental animal since they were large enough to allow a sufficient number of blood samples to be obtained yet small enough for the static exposure chamber employed. The animals were anesthetized by means of intravenous administration of nembutal and the carotid artery was cannulated with polyethylene tubing. A tracheotomy was performed to prevent any possible obstruction of air way. The animal was placed in the exposure chamber and the chamber sealed with the arterial cannula leading to the exterior. A blood sample was then withdrawn to establish the baseline condition. Halocarbon vapor was then admitted to the chamber in the desired concentration and blood samples were collected periodically during the exposure. Finally, the chamber was opened, effectively lowering the fluorocarbon concentration to zero, and blood samples were taken for several minutes thereafter. Halocarbon concentrations were then determined in the blood samples by the head-space analysis technique previously described. The results of two experiments, one with Halon 1301 and the other with Freon 116, are shown in Figure 3. The study with Halon 1301 showed that blood levels as high as about 15 μg/g were encountered during exposure to five percent atmospheric concentrations of the halocarbon. Our previous work had indicated blood levels of only about five μg/g immediately after exposure. The reason for this difference is apparent when one considers the rapidity with which blood levels followed changes in exposure conditions. Within 30 seconds of the time the animals were removed from the chamber, the blood level dropped from 15 μg/g to insignificant levels. This demonstrates the importance of obtaining a blood sample during the actual exposure to the halocarbon and not a few moments afterwards. Events during the start

HALOCARBONS IN BLOOD OF RABBITS
DURING 5% ATMOSPHERIC EXPOSURES

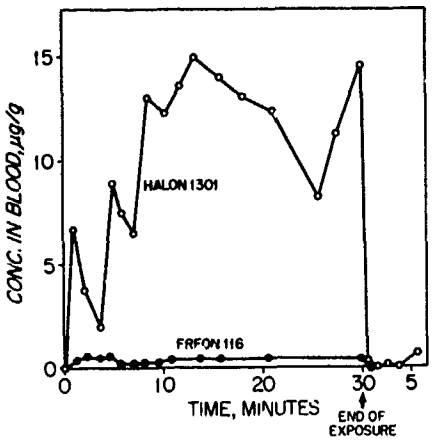


FIGURE 3. Halocarbons in blood of rabbits during 5% atmospheric exposures. Blood samples were withdrawn from the animals before, during and after exposures to either Halon 1301 (open circles) or Freon 116 (solid circles). Concentrations of the halocarbons in blood were determined by gas-liquid chromatography.

of the exposure were not so straightforward. Stabilized blood levels were not reached until about ten minutes after the start of the exposure. While it is conceivable that this period was required to establish an equilibrium condition within the animal, a more likely explanation is that the time was required to establish an equilibrium within the exposure chamber. Indeed, analysis of the air within the chamber at various points indicated that stable conditions were not achieved until after about 15 minutes. Contrastingly, at the end of the experiment, the animal was removed from the chamber, and admitted instantaneously to a stable (0 halocarbon concentration) atmosphere.

Data obtained during a similar exposure to Freon 116 at five percent showed less fluctuation during the initial stages of the exposure but more importantly demonstrated that the highest levels of this halocarbon reached in the blood of the animals during exposure was less than one µg/g. In fact, during exposure, the concentration ranged from 0.2 to 0.6 µg/g. As in the case of Halon 1301, blood levels of Freon 116 decreased to unmeasurable levels within one or two minutes after the animals were removed from the exposure chamber. We have also demonstrated a rapid equilibration and short half-life in rabbit blood with the gaseous fluorocarbon Freon 12. The results of a study with this compound are shown in Figure 4. In this study a circulating fan was incorporated into the chamber to establish as rapidly as possible a stable exposure condition. A short half-life in blood also has been demonstrated for Freon 11 (Patterson, Sudlow and Walker, 1971). A half-life of 0.5 to 1.5 minutes was measured in humans using pressurized aerosols of adrenergic bronchodilator drugs.

This laboratory is now undertaking studies of continuous exposure of laboratory animals to selected fluorocarbons. A 30-day exposure of rats to five percent Halon 1301 has recently been completed.

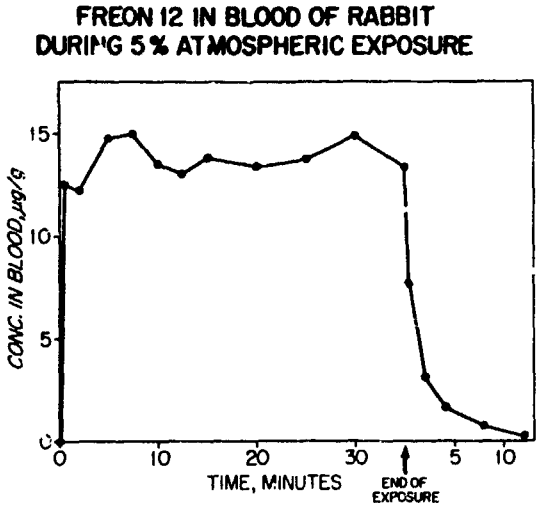


FIGURE 4. Freon 12 in blood of rabbit during 5% atmospheric exposure. Blood samples were withdrawn from the animals before, during and after exposure to Freon 12 and the halocarbon concentrations determined by gas-liquid chromatography.

In the study, the animals were exposed continuously for 23 hours each day in an environmentally-controlled exposure chamber. The remaining time each day was used for maintenance and animal care within the chamber. Extensive studies failed to reveal effects on serum electrolytes or hemotologic parameters including erythrocyte fragility in the exposed animals. As indicated previously, mitochondrial function was not altered.

Studies of blood did not reveal any accumulation of Halon 1301, as the material was apparently cleared from the continuously-exposed animals as rapidly as it was cleared from animals exposed only for a few minutes. There was no elevation in the rate of excretion of fluoride ion in the urine. There was some indication of elevated levels of liver enzymes although the results were not conclusive. Grossly, there was no pathology at autopsy and a thorough histological examination is underway. Currently a study is being conducted in which rats are being exposed in a similar manner to 20 percent Freon 116.

To summarize, a number of conceivable biological effects of selected halogenated hydrocarbons have been investigated in laboratory animals exposed briefly to the compounds. Similar studies are underway in continuously-exposed animals. With the exception of cardiac sensitization and within the limits of our exposure conditions, only minimal effects have been observed with the highly fluorinated compounds (Freon 116 and Halon 1301). While these observations support the general concept of biological inactivity of highly fluorinated compounds, one still hesitates to apply the term "biologically inert." Studies are planned employing procedures which, hopefully, will provide more sensitive probes into the biological action of fluorocarbons.

REFERENCES:

1. J. W. Clayton, "Handbuch der Experimentellen Pharmakologie," Vol. XX (O. Eichler, A. Farah, H. Herken and A. D. Welch, eds.), Springer, Berlin, pp. 459-500, 1966.

2. J. W. Patterson, M. F. Sudlow and S. R. Walker, "Blood-Levels of Fluorinated Hydrocarbons in Asmatic Patients After Inhalation of Pressurized Aerosols," The Lancet 2 (7724):565-568, 1971.

3. V. Ullrich and H. Diehl, "Uncoupling of Monooxygenation and Electron Transport by Fluorocarbons in Liver Microsomes," Eur. J. Biochem. 20:509-512, 1971.

DISCUSSION

Dr. Einhorn: I was just wondering -- you did not mention this, nor did any of the other speakers -- can you speculate if you have not run studies on what effects you might see at elevated temperatures and at elevated CO_2 levels, in combination with some of these fluorocarbons?

Dr. Griffin: No, I can't speculate on that.

Mr. Parker: When those values drop off after you remove the animal from the chamber, am I to take that to mean that the body itself frees itself in that time from the general concentration, or do I have Freon dissolved from the blood into the fat, and then gradually stored very stably in the fat, and I could have a very large concentration of Freon stored in the body with reprocessing in the direction of dissolving in the fat? That drop you see in the blood really does not measure the amount of Freon I have got dissolved in my various ganglia and nerve endings and so forth in the body.

Dr. Griffin: It does not necessarily mean that. We have done some studies with tissues other than blood. I am not as confident of the results yet, but our studies do not indicate any great storage of the gaseous fluorocarbons in tissues. By these, I mean specifically Freon 116 and Halon 1301. We did see some storage of 2402, at least for a 24-hour period.

Mr. Wands: I think in response to your question about body storage, Dr. Stewart has shown with various of the halogenated hydrocarbons, like the chlorinated compounds, that this varies tremendously depending upon the fat solubility of the compound and its vapor pressure. Some of the compounds, perchlorethylene, I believe, sticks around in the body so that there are trace levels detectable in the expired air for as long as 30 days after exposure.

Mr. Parker: The point I was making is that you simply cannot conclude from the data as given, that is, the rapid dropoff of the blood concentration without a prior knowledge of the fat solubility, that the fat tissues are free.

The reason I raised the question is pretty clear to me. I have tried to wash out of in situ preparations of heart or vagus muscle acetycholinesterase enzymes of these various materials, and it takes one at least a half hour to deliberately wash these out before you restore the acetylcholinesterase back to its original activity. So they are taken up and held by vital centers that are not reflected by the blood levels. This is generally true for a wide range of these materials, 1301 and the whole family. So I am simply saying that the blood level is not necessarily an indication after exposure of how much is stored. That is the only point I was trying to make.

Mr. Wands: You are quite right. There is no question about that at all.

Unidentified: On the same basis, couldn't you explain the reason why hexafluoromethane never attained any appreciable blood levels on the basis that it goes immediately into fat?

Mr. Parker: I think fat solubility has to be qualified here, too. It is not just a question of being able to rate them in terms of their organic fat solubility. It is a question of being able to fit into sites, but I think it would be interesting to sacrifice the animals as you went along, and see if you could relocate the concentrations in the body as they relate to the blood concentration. You have not done that yet, as I understand it.

Dr. Harris (NASA Manned Spacecraft Center): I believe part of the work was directed toward that in lipid membranes, both as to red cell fragility, and also the mitochondria. We believe it pointed specifically towards the absorption of this. I believe in partial response to your question about absorption into the fat membrane, the work on red cell fragility and the work on mitochondrial effects was directed towards that end. I think you did have incorporation into the lipid membrane. You would expect to see changes in the biological activity of that membrane.

Mr. Parker: My comment was directed to the fact that in the case of exposure in situ, vagus nerve assemblies, and watching the action of in situ acetylcholine, and that obviously must involve the phospholipid membrane, it takes about 45 minutes to actually wash the material out before it is restored to its normal activity. So I am arguing about it being bound to the fat bodies associated with the membrane by some complexing process, which I think the action probably is.

Dr. Griffin: I might mention that even though there was a rapid decrease shown, there was a little bit of remaining material there, but barely above our base line level.

Mr. Parker: Did that continue for some time?

Dr. Griffin: It continued for about 10 or 15 minutes. But this amount was so small that we were very hard pressed to measure it.

Dr. Torkelson: I think you will find in your studies that unless you take these animals out for 24 or 48 hour exposures in which you are close to equilibrium conditions, you are going to have so much dynamics going on, shifting from one organ to the other, that data would be virtually impossible to interpret.

I would also like to caution on fat solubilities. What is fat?

Mr. Parker: That is my point.

Dr. Torkelson: If you extract liver and kidney, you get virtually the same fat content -- I think it is four percent -- yet there is a difference of eight-fold on the equilibrium concentration of methyl chloroform towards these two organs. So it is not just fat solubility you are talking about. You are talking about proteins which are organic. You are talking about a lot of other components that are organic.

I would like to make a comment here to Dr. Harris that just because he exposed his system to an equal volume of gas flow through, the data here on the blood concentration indicates that those tissues may not have been exposed to anything comparable to an equal molecular solution. There may have been a thousand times as much of the 1301 dissolved in the solution as there was Halon salts.

Mr. Wands: I think that was clear in Dr. Harris' comments.

Unidentified: Do you have any evidence for storage of 116 in any body tissues?

Dr. Griffin: We have not developed procedures, and I have not seen the procedures alluded to for tissues other than blood.

GENERAL DISCUSSION OF SESSION II

Herbert E. Stokinger

National Institute of Occupational Safety and Health

Dr. Stokinger: The time is rather short. As I see my role here, it is not to summarize, contrary to the opinion of some here, but to lead the discussion by pointing to some things that have occurred to me that have not been discussed.

First, I would like to convey a message that was given to me personally by one in the audience. What he wanted, I guess, was an overview of the toxicologic detail that was leading to a little confusion in his mind, and he would like to hear a comparison of the toxicologic effects and toxic hazards of the various fire extinguishing halocarbons for man in different kinds of fires. This is from the practical standpoint, for example, of 1301 versus 1211 in England and 2402 in Italy. He asks which is the more useful for different kinds of fires. Although this may seem an easy question to ask, if you consider that the pyrolysis problems from different kinds of fires are different, it seems almost impossible to generalize. But perhaps there are some people expert enough in this audience -- I see Ken Back smiling as though he can answer this right away, and maybe Dr. Clark can contribute something, and Dr. Reinhardt and perhaps others. In short, I think he wants to know where we have been and where are we going for the practical man in the field. Is anyone timorous enough to address himself to this practical question of which among the fire-fighting agents we have here would be the most appropriate for certain kinds of fires? It is a very practical question.

Unidentified: This is a question for tomorrow.

Dr. Stokinger: All right. Maybe we can consider this a little untimely, then.

Since time is short, did I hear that Dr. Carhart wanted to start the general discussion?

Dr. Carhart: There may not be an answer to this question, either. We are concerned about the toxicity of the materials of which the Halons themselves are composed. I would like to throw a general question out. Has anybody seen any unsaturated fluorocarbons in any of the pyrolysis products or heat-treated products of these materials?

Maybe I ought to ask the following question, a corollary question. Has anybody really looked for them? The toxicity of these I guess is pretty high.

Dr. Stokinger: I may be able to contribute a little bit to that, although I have never handled these halocarbons as such, but more or less ones in plastic or polymerized form. But it seems that you can make a dichotomy very clearly, whether these substances pyrolyze in the presence of oxygen. I am thinking now of teflon, in which case you get carbonyl fluoride as one of the major products. However, if you decompose or pyrolyze the same material without air or oxygen present, you get unsaturated linkages. So it is as simple as that, I think.

Dr. Carhart: I still pose the question, has anybody ever seen any or have any people looked for them chemically?

Dr. Stokinger: Well, du Pont has found this for teflon.

Dr. Carhart: I am not so concerned about teflon.

Dr. Stokinger: It is a polyfluorinated hydrocarbon.

Dr. Carhart: I guess really what I am fishing for is are any of the toxicological effects of material that has been pyrolyzed or heat-abused due to that material in addition to the carbonyl fluoride and HF?

Mr. Ford: We have looked very cursorily for a variety of types of materials which are formed upon decomposition of 1301 under fire conditions, and we have not found significant quantities of materials other than hydrogen fluoride and hydrogen bromide. The carbonyl fluorides, free bromine and many other materials which could be proposed as being formed have not been found at all. This was done with a gas chromatograph which should have been capable of isolating and possibly identifying materials other than these three. But for 1301, at least, we have not seen materials beyond the HF and HBr. The level of sensitivity would have been in the neighborhood of something like a tenth of a part per million.

Mr. Parker: I guess I can comment on that if you will accept an indirect comment with regard to the agent. We have looked at the oxidation of teflon, which has a tetrafluoroethylene precursor in the gas phase. The result I wish to report to my friend at du Pont is the nature and ratio of the pyrolysis products varies with the oxygen partial pressure. It seems to turn out that oxygen at low partial pressures, say as in an air environment from the space point of view, tends to give much larger concentrations of toxic species than it would at higher oxygen partial pressures, where one gets, I might add, complete combustion. I don't think it is a clear answer to Carhart's question, because fundamentally you have three interactions. I can think of maybe 20. But if the Halon collides with the surface, as our friend from Italy discussed, it is entirely possible that there could be catalytic reactions which could induce isomerizations which would give rise to unsaturated compounds. There certainly is evidence for that in the thermal decomposition of compounded fluorinated plastics that you could change the entire direction of the pyrolysis process by compounding it, so I think we have seen unsaturated compounds when we have compounded teflon with mica and other

kind of fillers, changing the direction of the polymerization; we most certainly have seen a higher population of COF_2 and HF in the case of teflon which has been decomposed at lower oxygen partial pressures in the case of our experiments in polymers. I can't comment on the polymers themselves.

Dr. Torkelson: If you got the methane, you would have to have a recombination to get an ethane before you could have any unsaturation. It seems rather unlikely.

Mr. Ford: The chemistry is all against you, John. In working with teflon, you are decomposing the material and getting a batch of unsaturated monomers. This is the natural course of events. In the case of the decomposition, if you want to call it that, of the extinguishing agent, you are attempting to perform a chemical synthesis at the same time you are performing a chemical decomposition, and it just does not work out that way. If you will look at some papers that were published by Atkinson, he talks about the kinetics of the formation of tetrafluorethylene, tetrafluorpropylene, and so on, and the numbers are such that if you just look at the decomposition numbers of the extinguishing agent itself, you wind up with --

Mr. Parker: I am not making my point. I have personally decomposed the polymer of fluorethylene and I get very distinct fluorethane, COF_2 and DHF from dehydrofluorination, and so forth, in the presence and in contact with surfaces such as magnesium oxide filler. I get mass numbers in my mass spectrometer of fragments which have molecular wiights of the order of 200 and 300, every mass number that is populated, and I say that there is a possibility of synthesis occurring by collision and recombination of surfaces. That is what I have said. That is what I see in the spectrometer.

Mr. Ford: You are not seeing the synthesis. You are seeing decomposition in the spectrometer.

Mr. Parker: I see a redirection of the decomposition as a consequence of collision with surfaces or the presence of wall effects.

Dr. Stokinger: Let us not get into fisticuffs here. How much longer do you think we ought to pursue this discussion. We have just barely begun, and have used half of the time already.

Dr. Einhorn: I would like to suggest that the pyrolysis of the fluorocarbon may be entirely different from what you find from a fire. If you are applying it to a hydrocarbon fire, for example, I can conceive of getting interactions between the fluorocarbon or its decomposition products and the products from the fuel that could lead to an unsaturated halogen compound, and some of these we know are highly toxic. This morning, for example, we were shown that acrolene is an important product in certain fires, and in the presence of a decomposing halocarbon, I can conceive of getting halogenated aldehydes which we know are extremely toxic and irritant compounds.

Dr. Stokinger: Very good. Ken, did you have something to say?

Dr. Back: I don't want to change the subject too much, but I thought I would take a stab at part of that first question. That was what is the relative toxicity of the compounds that we are talking about: 2402, 1211, 1301 and 1011, or CB. I think this brings us back to what I said before, and that is that we can't talk about straight toxicity any more, but rather about hazard. There is a great difference between toxicity and hazard. If I put them on the basis of that which each of them will do to arrhythmogenic changes in the heart, then I would have to say that in the order of toxicity, now, built on percentage inhaled, that chlorobromomethane would be the most "toxic." It causes an effect somewhere between 0.5 and 0.6 percent, less than one percent.

Then you would have to say 2402 would be next because it produces the same effect at around 1.5 percent. Then would come 1211 at around 14 or 15 percent, and then would come 1301, somewhere above 50 percent, if you will. This is in the same species.

Now, that is on the basis of actually getting that amount into an animal at a given time, but that is not what the hazard is, because I don't know of a single fireman that has ever been killed by chlorobromomethane, unless he was run over by a truck carrying it, from cardiac arrhythmias, now, or from any other causes, for that matter. I don't know of a single instance, and we have certainly firemen in the Air Force who have been exposed to it to the point of getting it ingested by having a hose sprayed right in their faces. One of them was out on Guam, I believe. He must have swallowed a number of cc's of the compound. This did not knock him off because of liver damage, either, which you would expect certainly on oral ingestion of the compound.

The point of the matter is that the effects that we are talking about here are No. 1, I think you have to worry about arrhythmias, and No. 2, you have to worry about decreases in blood pressure. No. 3, you have to worry about central nervous system depression.

In terms of hazard, perhaps 1301 is the most hazardous, because it is the most volatile. Perhaps CB is the least hazardous, because it is the least volatile of the compounds you are talking about. When you spray it on a fire, you are spreading a single stream, or at least a well-defined stream onto a fire, and the chances of the man being exposed to a half percent by volume in air is rather limited, whereas if you are taking the size of an A-20 extinguisher with 1301 and spraying it into a fire, you have a chance of greater volatility, and therefore a chance of getting above our required five percent for five-minutes level. You all know that we have got humans exposed here up to ten percent without any great problems. It is when you get above ten percent that you have got to worry about the occasional individual who is going to have an arrhythmia.

So we have to start rethinking about how we are going to classify these agents, and on what basis you are going to take your classifications.

Dr. Bauman: I would like to offer something to support Dr. Back's comments. Dr. Clark in his talk showed a slide that had a 5-A Underwriters' Laboratories rating for 1211 and for carbon dioxide. Missing from that table is the application of that data to use. In my talk I showed that it took eight times as much carton dioxide by volume to control a fire as it does 1211. The exposure to people is in the end use fire environment, and carbon dioxide has been with us for many years. It has killed some people who entered rooms a long time after where the CO_2 had stayed because of no ventilation or improper ventilation. The Coast Guard has some stories of this nature. But there have been many hundreds and hundreds of thousands of uses of CO_2 extinguishers and CO_2 fixed systems that were highly successful. And CO_2 certainly is to some degree seriously toxic.

Now, I would direct to the doctors who spoke this afternoon that we got no comparison for use as to how your studies relate to the things that have been happening out in the market place for these many, many years.

The other one would probably be carbon tetrachloride. I don't know how many years that was around, but it has put out many, many fires. It is bad, but how many times were there deaths from carbon tetrachloride? I think Stan Auck mentioned a few. I don't know how many there are totally out of the number of usages. But it must be that the probability of exposure is something like Dr. Back is outlining. I think you have to put these things into some context as to the probability of exposure. You are trading off again a value in extinguishing operations for a risk or a hazard. There are many other hazards that manufacturers or owners of extinguishers might be concerned with, such as corrosion, contamination, and so forth. At the moment we are addressing ourselves to life safety, and in this respect how many lives are saved by proper effective and efficient use of, for instance, carbon dioxide extinguishers?

Now, when you start talking about how 1211 is substantially superior in effectiveness, isn't it logical therefore that there is a net effective gain in the use of 1211 over CO_2?

Dr. Stokinger: Is there another question?

Mr. Wilson: Over the last four years we have seen dramatic abilities of these agents, 2402, 1211 and 1301, to change our ability to control fires. There are at least a hundred human exposures to fire extinguishing tests as the fire was lit, during the growth of the fire, and during the extinguishment at concentrations between three and eight percent that I personally know of with 1301. I personally have experienced no added hair growth because of exposure to 1301, and my sexual potency has not improved greatly because of exposure to 1301. But I have listened with great interest this afternoon particularly to Drs. Reinhardt, Clark and Call, with measured experiments on these agents. I would like to ask the question, is there any one of those three gentlemen who knows of any residual effect to any part of the body one week after exposure to those three agents?

Dr. Clark: Since I was one of the subjects for exposure to 1211 on two or three occasions, I can testify there is absolutely no effect on any functions of the body even ten minutes after cessation of exposure.

Dr. Stokinger: Is this because the material does not stay in the body?

Dr. Clark: With the short exposures we are talking about, there is very little retention.

Dr. Call: The only thing I would say to that is certainly there were no adverse effects at all. We had one chief petty officer who always wanted to be exposed on his bowling night. He said he always bowled better after the treatment.

Dr. Stokinger: I think we will have to close the meeting for today. I want to thank the speakers and the discussants. We will reconvene tomorrow at 8:30.

III APPLICATION SESSION

Chairman, Carl W. Walter

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REMARKS

Dr. Walter: I would like to share with you a nugget that came into my hands last evening. It is the paper of Shuzo Yamashika, from the Fire Defense Agency, the Fire Research Institute, Ministry of Home Affairs, in Tokyo. I have visited this laboratory annually for the last three or four years and watched this research develop. The paper is 17 pages, of which 14 pages are data, one page of definitions, and two pages of discussion. I can summarize it best by reading the title: "The Dependence of Extinction Time and Decomposition of Halogenated Extinguishing Agents on Its Application Rate." He shows by both wood crib fires and hexane PAM fires in both open and confined spaces that the more rapidly the proper concentration of the various halons are applied, the less in the way of degradation products, pyrolysis products, he could identify.

I thought I would begin todays's deliberations with that brief summary of his work, because it seemed to fit with the end of the program yesterday.

The first paper this morning, "Extinguishment of Surface and Deep Seated Fires with Halon 1301," will be given by Charles L. Ford of the du Pont Company.

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EXTINGUISHMENT OF SURFACE AND DEEP-SEATED FIRES WITH HALON 1301

Charles L. Ford

E. I. du Pont de Nemours & Company

The effectiveness and effects of applying Halon 1301 to fires is widely debated. Indeed, the purpose of this symposium is to offer a forum for debate of the halogenated extinguishing agents. But whereas debate in the past has been conducted largely without benefit of specific knowledge, and what specific knowledge was available has often been applied grossly out of context, this symposium will hopefully accomplish three broad objectives:

1. Bring to the fore, if only in summary form, current knowledge on halogenated agents,

2. Produce debate in light of current knowledge, and

3. Most important of all, provide context for future debate and investigation.

As for my contribution today, I intend to review the Halon 1301 requirements which have been determined for a variety of fuels and the extent of agent decomposition which may be expected from a variety of fire extinguishment situations. Since this is not one subject but two very broad ones, the discussion will necessarily be limited to the one agent, Halon 1301, to one type of application, namely total flooding, and to two types of extinguishment situations, i.e., extinguishment of flames and deep-seated fires. Thus, I will not discuss other halogenated agents, nor local application, nor use of hand portable extinguishers, nor the concept of "inerting." But even narrowing the subject in this way will only permit a superficial treatment.

EXTINGUISHING EFFECTIVENESS

First, we will review the effectiveness of Halon 1301 against two broad classes of fires: flammable liquids, and flammable solids.

Flammable Liquids

The National Fire Protection Association Standard on Halogenated Fire Extinguishing Agent Systems -- Halon 1301 No. 12A-1971 (1) lists Halon 1301 concentrations to extinguish thirteen fuels (ethyl alcohol is listed also as commercial denatured alcohol), as presented in Table 1.

TABLE 1

Halon 1301 Design Concentrations for Flame Extinguishment

In Air at 1.0 Atm. and 70°F

Material	Minimum Design Concentration* % by Volume
Commercial Denatured Alcohol	4.0
n-Butane	2.9
i-Butane	3.3
Carbon Disulfide	12.0
Carbon Monoxide	1.0
Ethane	3.3
Ethyl Alcohol	4.0
Ethylene	7.2
n-Heptane	3.7
Hydrogen	20.0
Methane	2.0
Propane	3.2
Kerosene	2.8
Petroleum Naphtha	6.6

* Includes a safety factor of 10% minimum above experimental threshold values. For other temperatures or pressures, specific test data shall be obtained.

The "flame extinguishment" concentration implies that the given fuel is burning and that Halon 1301 injected into the air surrounding the fuel at the stated concentration will extinguish the fire. The further condition of diffusion flames applies, i.e., that the flames emanate from pure fuel vapor, with the oxygen supply diffusing into the flame zone from the outside. These data are not applicable to premixed flames, nor to "explosive" mixtures of fuel vapor in air.

At this point, it might be useful to look at the source of the data which comprise this table. This is shown in Table 2, taken from a memorandum circulated to the NFPA 12A Committee in 1967 (2). Also shown is a recent value for marine diesel fuel (3), not yet included in the 12A Standard. There were five contributors to these data, separated both in time and methods of evaluation. The diffusion flame data were obtained in laboratory-scale equipment. Pan fire data were obtained on fires of at least one sq. ft. area (in the Factory Mutual tests, up to ten sq. ft.). In establishing values to be included in the 12A Standard, the Committee selected the larger-scale pan fire data where available. For several fuels, only laboratory diffusion flame data were available,

which still have not been superseded by pan fire data. Little data on flammable liquids or gases have been added to the list during the past five years. A project is underway to reevaluate these and about twenty other fuels under consistent large-scale conditions, but no data are available from the study.

Flammable Solids

Recent investigations have focused on the effectiveness of Halon 1301 total flooding systems on Class A, or flammable solids, fires. At the time the 12A Standard was first published in tentative form in 1968, all Class A fires were treated more or less equally, using data which had been obtained on a charcoal configuration at Factory Mutual Research Corporation. This treatment recognized a relationship between the Halon 1301 concentration applied to the fire and the time required for the fire to be completely extinguished. When the agent is first applied to a charcoal fire, the flames are immediately extinguished; but the glow, or deep-seated combustion, continues. If the enclosure then is ventilated, the fire will rekindle. But if the agent concentration is maintained around the fuel bed, the glowing combustion gradually subsides and finally ceases altogether. This additional time is termed "soaking" time and, at least for charcoal, was found to be dependent upon the applied concentration. Using higher concentrations permitted the use of shorter soaking times. This effect is illustrated in Figure 1.

Comparison of the small amount of other Class A data available at that time to the concentration-soaking time curve for charcoal indicated that the charcoal curve was representative of other deep-seated combustion (4). As more types of flammable solids were studied, however, it became apparent that the charcoal curve did not always hold. The testing laboratories have decided that for most practical applications, a ten-minute soaking time is the maximum that should be expected. Shredded paper placed loosely in an open wire basket and ignited at the bottom center requires about 20 percent Halon 1301 for extinguishment within this ten-minute limit. Closely spaced parallel panels of low-density compressed fiberboard and multiple-layer corrugated cardboard require concentrations approaching 30 percent to obtain complete extinguishment. As illustrated in Figure 1, these requirements are well in excess of those for charcoal. In light of this, the Halon 1301 requirements for solid fuels in Standard 12A were rewritten in 1970 and appear in the 1971 edition. The charcoal curve was removed from the standard and a general discussion of the factors which tend to produce deep-seated fires substituted. The definition of a deep-seated fire was included, which is as follows:

> "...if a five percent concentration of Halon 1301 will not extinguish (the fire) within ten minutes of application, it is considered to be deep-seated." (Parenthesis added)*

* NFPA Standard No. 12A-1971, Paragraph A-2400.

TABLE 2

Flame Extinguishment Determinations with Halon 1301

Fuel	Diffusion Flames		Pan Fires			
	Creitz (9)	"Freon" Products Laboratory (10, 11)	Factory Mutual (12)	Fyr-Fyter (13)	"Freon" Products Laboratory (3, 14)	Douglas (15)
Hydrogen	17.7					
Methane	1.5	1.53				
Ethane	3.0					
Ethylene		6.				
Propane	2.7					
Isobutane		3.				
n-Butane	2.4					
n-Heptane		3.(w)	3.3	3.97*		
Kerosene						2.5
Ethanol			3.6			
Carbon Monoxide	0.8					
Carbon Disulfide		12.(w)				
Petroleum Naphtha					6.*	
Marine Diesel Oil					4.4	

* - Calculated from reported flooding factors.

(w) - Fuel introduced into combustion chamber by wick.

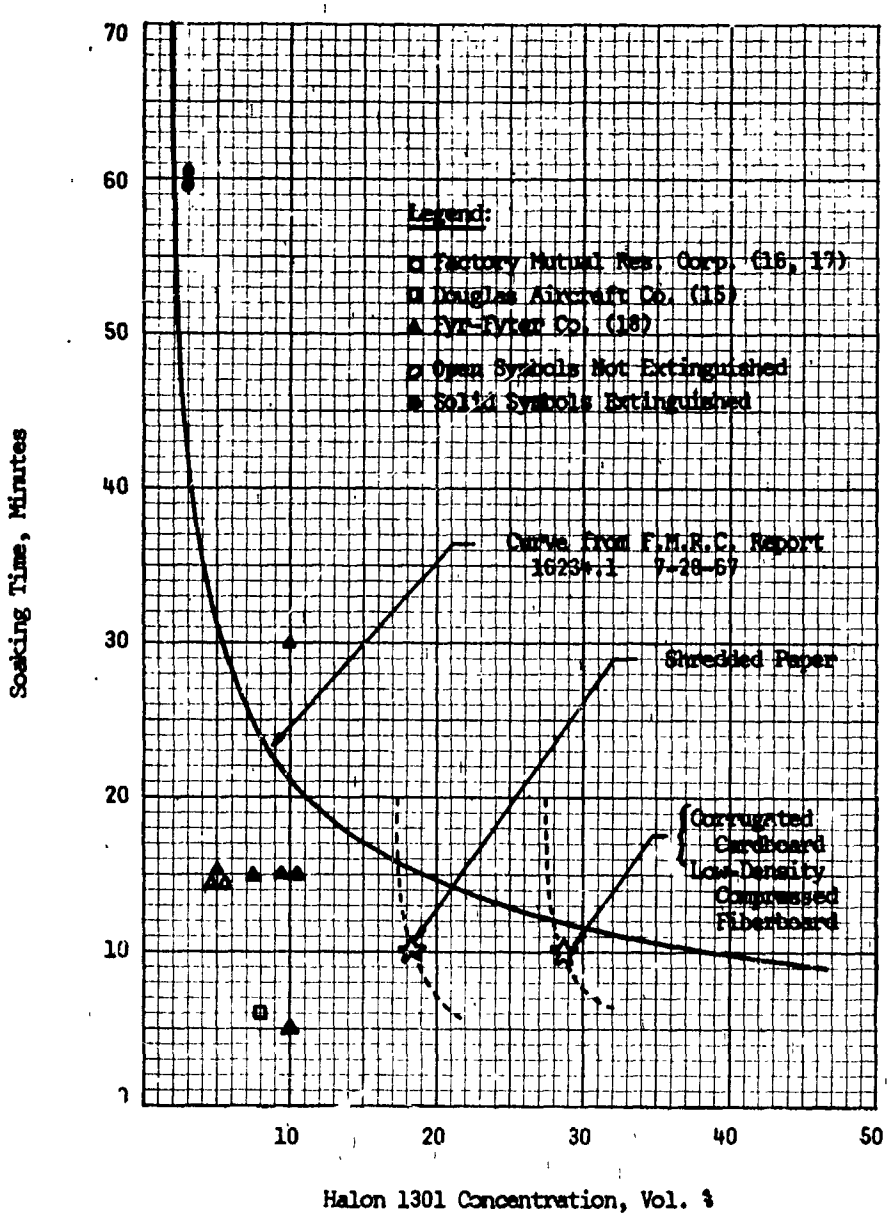


FIGURE 1. Soaking Time vs. Halon 1301 concentration for deep-seated fires.

This definition has served to guide recent tests on Class A fuels. Table 3 lists the major flammable solids that have been investigated to date and classifies the results according to surface or deep-seated extinguishment characteristics.

It has been observed in these tests that fuel configuration or arrangement is an important variable affecting the tendency of a fuel to produce deep-seated fires. For example, fires in shredded paper which is piled loosely on the floor or placed in solid-wall waste containers are completely extinguished with a five percent concentration

TABLE 3

Extinguishment of Flammable Solids Fires with Halon 1301

	Halon 1301 Concentration, % (Vol.)					
	Factory Mutual (17)	Fenwal (8)	Ansul (8)	du Pont (8, 19)	Safety First (20)	Underwriters' Labs (21)
Surface Fires						
Polyvinyl chloride		2.0		2.6	3.8	
Polystyreme)		3				
Polyethylene)						
Stacked computer printout paper			5.1			
Polyester computer tape - wound		5			3.8	
Wood crib 30 pcs. 3/4 x 7/8	3					
Wood crib 24 pcs. 2 x 2 x 18					3.8	
Wood crib 1A 50 pcs. 2 x 2 x 18					3.8	3.88
Excelsior loose on floor					3.8	6.0
Shredded paper loose on floor					3.8	
Polyurethane foam				3	3.8	
Cotton lint					3.8	
Crumpled paper	3	6			3.8	
Wood pallets - stack of 10	3					
Deep-Seated Fires						
Shredded paper in wire basket					20	18.0
Polyester computer tape loose in open wire basket		10				
Charcoal	13					
Parallel wood blocks	20					
Glazed fox fur					6.5	

of Halon 1301 within a ten-minute soaking period. If the shredded paper is placed in an open wire basket elevated approximately six inches above the floor and ignited at the bottom center, the fire rapidly becomes deep-seated, requiring a Halon 1301 concentration of about 17 percent by volume for complete extinguishment. When ignited at the top or on a side, the fire is often extinguished completely with a five percent concentration. Loose polyester-base computer tape in an open wire basket similarly produces deep-seated fires; but when wound tightly on reels, as during typical use and storage, fires exhibit surface-burning characteristics only. Some materials show no tendency toward deep-seated fires. These primarily are thermoplastics, such as polystyrene, polyethylene, polyvinyl chloride, and polyurethane materials. However, even where the fire has become deep-seated, application of a low Halon 1301 concentration has two benefits. First, all flaming combustion is halted, preventing rapid spread of the fire to adjacent fuels. Second, the rate of combustion is drastically reduced. These two characteristics give effect to the concept of "control" of deep-seated fires.

The present industry approach regarding flammable solids fires is to determine which fuels and configurations can realistically be expected to remain as surface fires and which ones will become deep-seated. In essence, this is a cataloging effort. This knowledge will permit the designer of a given system to evaluate the hazard to be protected in terms of the capabilities of Halon 1301. If the hazard contains only materials known to exhibit surface burning, then provision of a low concentration of Halon 1301 may be expected to extinguish the fire completely. If a deep-seated potential exists, then the designer must provide either a much higher concentration of Halon 1301 or a supplementary means of extinguishing the deep-seated fire. Two considerations generally lead to the latter choice: (1) Halon 1301 is a relatively expensive agent, and use of concentrations as high as 20 to 30 percent are uneconomical; (2) Since one of the unique properties of Halon 1301 is its high degree of safety to personnel in low concentrations, design concentrations of 20 to 30 percent erase this major advantage. The means which the designer should use to handle a deep-seated fire will depend upon individual characteristics of the hazard. Notification of a local fire department or provision of other automatic means, such as water sprinklers, are possible solutions.

HALON 1301 DECOMPOSITION

A controversial characteristic of Halon 1301 is its potential thermal decomposition upon application to a fire. At least one theory of extinguishment requires this decomposition to produce bromide radicals, which then tie up active intermediate combustion products into less active species. But whether actually required or not, the phenomenon does occur and has been observed to some degree in virtually every fire extinguished by Halon 1301. The by-products are predominately hydrogen fluoride, HF, and hydrogen bromide, HBr. Lesser quantities of bromine (Br_2) and carbonyl halides (COF_2 and $COBr_2$) have been reported; but in light of recent studies (5, 6) their presence is questionable. One common characteristic of these materials is their irritating odor. The nose can easily detect these compounds in concentrations

of only a few parts per million by volume. Hence, they give the observer an intuitive feeling that a highly toxic hazard exists, when such is not necessarily the case. On the positive side, they provide an olfactory alarm to warn the unintentional intruder that a hazard may exist. The primary hazard may not be due to Halon 1301 decomposition products. Oxygen depletion and carbon monoxide, less irritating and equally toxic hazards present in most fire situations, are certainly more difficult to detect.

Analysis of atmospheres following extinguishment of fires with Halon 1301 has been attempted in several instances with flammable liquid, solid surface, and deep-seated fires. Rather than attempt a complete review of data collected to date, three rather typical situations will be discussed in which these types of fires have been studied.

Flammable Liquid Fires

Three sizes of flammable liquid fires using n-heptane fuel were investigated in a series of twenty-five extinguishment tests by du Pont (7). The purpose of the tests was to study the relative effects of fire size, fire preburn time, and agent discharge time on the quantities of decomposition products formed. The data collected from this series of tests are shown in Table 4. Although the effects of each variable could not be determined precisely, several general observations are possible. With small fires, i.e., 0.06 sq. ft. burning fuel surface per 1,000 cu. ft. enclosure volume (ft.^{2}/MCF), the quantities of all decomposition products were minimal -- less than five ppm by volume each of HF, HBr, and Br_2. At larger fire sizes, 0.6 ft.^{2}/MCF, HF concentrations ranged from less than five ppm to about 250 ppm; HBr concentrations ranged from less than five ppm to just over 50 ppm; Br_2 was not detected at an analytical sensitivity of 0.3 ppm. There was a general tendency for longer preburn times and longer agent discharge times to produce higher HF and HBr concentrations, although HF concentrations at the 23 second discharge time were somewhat lower than at the 14 second level. This effect is not readily explained, but it has been observed in other test series.

In the very large fires, 6 ft.^{2}/MCF, the thirty-second preburn level was eliminated in order to prevent the fire from consuming the test enclosure. Immediately after ignition, flames occupied a substantial portion of the enclosure volume. As expected, concentrations of Halon 1301 decomposition products resulting from extinguishment of these fires were about an order of magnitude higher than at the 0.6 ft.^{2}/MCF level. Hydrogen fluoride ranged from about 300 to about 2,000 ppm. Hydrogen bromide ranged from about 40 to about 600 ppm. Again, bromine was not detected. The concentrations of both HF and HBr were higher at longer discharge times.

From these tests, it appears that Halon 1301 extinguishing systems installed to protect flammable liquid hazards, in which the fire can spread rapidly, should be capable of both detecting the fire rapidly, and discharging the agent quickly. The NFPA Standard 12A requires an agent discharge time of ten seconds or less, in order to minimize agent decomposition. Lest the high HF and HBr concentrations

TABLE 4

Halon 1301 Decomposition Produced by n-Heptane Fires

1,695 Cu. Ft. Enclosure Volume
4% Halon 1301 Concentration (Vol.)

Test No.	Fire Pan Size, Sq. Ft.	Ratio of Fuel Area to Room Volume Ft. 2/1,000 Cu. Ft.	Preburn Time, Seconds	Halon 1301 Discharge Time,* Seconds	Flame Ext. Time,* Seconds	Decomposition Products PPM by Volume in Air		
						HF	HBr	Br_2
1	0.1	0.06	0	23.0	11.5	1.8	3.5	<0.3
2	0.1	0.06	30	23.0	15.4	1.3	2.9	<0.3
3	0.1	0.06	0	13.5	7.6	0.9	1.6	<0.3
4	0.1	0.06	30	13.5	7.1	1.8	2.1	<0.3
5	0.1	0.06	0	5.7	4.0	<0.1	2.9	<0.3
6	0.1	0.06	30	5.7	4.8	1.4	2.8	<0.3
7	1.0	0.6	0	23.0	36.8	108.	12.	<0.3
7A	1.0	0.6	0	23.0	20.0	81.	13.	<0.3
8	1.0	0.6	30	23.0	24.5	230.	59.	<0.3
8A	1.0	0.6	30	23.0	21.4	230.	44.	<0.3
9	1.0	0.6	0	13.5	13.5	79.	20.	<0.3
9A	1.0	0.6	0	13.5	12.7	46.	18.	<0.3
10	1.0	0.6	30	13.5	12.6	243.	41.	<0.3
10A	1.0	0.6	30	13.5	11.5	211.	19.	<0.3
10B	1.0	0.6	30	13.5	11.8	183.	19.	<0.3
11	1.0	0.6	0	5.7	5.8	12.8	4.4	<0.3
11A	1.0	0.6	0	5.7	4.7	8.4	2.8	<0.3

12	1.0	0.6	30	5.7	5.3	122.	18.	<0.3
12A	1.0	0.6	30	5.7	6.7	151.	18.	<0.3
13	10.0	6.0	0	25.0	21.6	1,664.	588.	<0.3
13A	10.0	6.0	0	25.0	20.0	1,907.	397.	<0.3
14	10.0	6.0	0	15.0	13.0	1,101.	191.	<0.3
14A	10.0	6.0	0	15.0	16.3	1,208.	382.	<0.3
15	10.0	6.0	0	6.0	10.0	666.	112.	<0.3
15A	10.0	6.0	0	6.0	5.2	320.	38.	<0.3

* - Measured from discharge start.

Source: Reference 7

observed with the large fire cause concern, it should be realized that the area would not be survivable due to the size of the fire alone. It is doubtful whether humans could survive even the 0.6 ft.^{2}/MCF fire alone.

Flammable Solids Surface Fires

Solid surface fires were examined by Fenwal, Inc., in a recent industry program in which the suitability of Halon 1301 total flooding systems for computer rooms was examined (8). A fuel array was constructed of twenty-four empty polystyrene reels and eight empty polystyrene cases, as used to contain magnetic computer tape. Twelve of the empty reels were fitted with polyethylene sealing bands. These components were arranged on two shelves of a commercial storage rack for computer tape. Four fire tests were performed with this fuel array in a 1,536 cu. ft. enclosure, all employing a three percent (vol.) Halon 1301 concentration and a ninety-second preburn time. Agent discharge time was the independent variable, ranging from 1.2 seconds to 19 seconds. The results of gas samples for HF and HBr analysis are shown in Table 5. Hydrogen fluoride ranged from about 12 to 30 ppm. HBr ranged from about 24 to 50 ppm. There was no distinct tendency toward higher decomposition levels at longer agent discharge times, as was observed with flammable liquid fires. The absolute values of both compounds produced in this test series were quite low, yet the fire was large enough to produce interior temperatures in excess of 500°F within five minutes of ignition. Slow-burning flammable solids thus do not appear to require the same rapid detection and agent discharge capabilities of Halon 1301 systems that are placed on flammable liquid hazards.

Flammable Solids Deep-Seated Fires

Deep-seated fires in flammable solids were investigated by Ansul Company in the previously mentioned industry computer fire test program (8). The fuel was an assortment of computer printout paper, data tabulating cards, and paper punch tape arranged randomly in an open wire basket. This arrangement previously had been demonstrated to produce a deep-seated fire. The fire preburn, defined as the weight of fuel consumed during the preburn period expressed as a percent of the fuel consumed in prior free burn tests, was varied from 25 percent to 50 percent; and Halon 1301 concentration varied from 5.1 to 21 percent (vol.). The results of gas analyses for HF and HBr concentrations obtained at various times during each test are shown in Table 6.

SUMMARY

Low concentrations -- four to six percent -- of Halon 1301 are capable of extinguishing a wide variety of flammable liquid and surface-burning solid fuels and of controlling deep-seated fires in flammable solids. In extinguishing or controlling fires, decomposition of Halon 1301 appears to occur, other factors being equal, in proportion to the size of the fire and the length of time in which the agent is in contact with the flames or glowing embers. In properly designed extinguishing systems, agent decomposition can be minimized to the point

TABLE 5

Halon 1301 Decomposition Produced by Surface Fires in Flammable Solids (Fenwal, Inc.)

Twelve Empty Polystyrene Reels
Eight Empty Polystyrene Cases
Twelve Empty Polystyrene Reels with Polyethylene Bands
1.5 Min. Preburn Time
3 % (Vol.) Halon 1301 Concentration
1,536 Cu. Ft. Enclosure Volume

		Mean[1] Concentration, PPM (Vol.)							
	Test No.	F-19		F-20		F-21		F-23	
	Discharge Time, Sec.	1.2		7		11.5		19	
		HF	HBr	HF	HBr	HF	HBr	HF	HBr
Sampling Time [2]:	<1 min.	31	33	18	18	13	50	38	32
	5 min.	29	35	18	23	10	56	26	56
	10 min.	52	24	13	24	12	49	19	40
	15 min.	27	27	19	27	11	62	24	46
	20 min.	21	25	14	25	11	39	24	32
	25 min.	21	23	18	23	12	47	27	47
	30 min.	23	24	10	21	11	44	18	42
Grand Mean		29	27	16	24	12	50	25	42

(1) - Mean of samples taken at two heights in enclosure.
(2) - After completion of discharge.

Source: Reference 8

TABLE 6

Halon 1301 Decomposition Produced by Deep-Seated Fires (Ansul Company)

Five Lbs. Printout Paper, Tabulating Cards, and Paper Tape Randomly Assorted in 18" Dia. x 30" High Open Wire Basket 1,729 Cu. Ft. Enclosed Volume

	Mean[1] Concentration, PPM (Vol.)											
Test No.	A-15		A-16		A-18		A-24		A-25		A-26	
Preburn, % by Weight	50		25		25		50		50		50	
Halon 1301 Conc. % (Vol.)	5.1		5.1		5.1		5.1		11.8		21.0	
Discharge Time, Sec.	2		2		2		2		4		8	
	HF	HBr	HF	HBr	HF	HBr	HF	HBr	HF	HBr	HF	HBr
Sampling Time[2]: <1 min.	7	9	12	23	13	5	9	16	3	6	5	4
5 min.					15	4	8	11	2	3	7	3
10 min.	10	21	11	17	14	4	11	17	3	4	6	3
15 min.					19	6	9	17	9	6	5	3
20 min.					16	6	8	9	7	6	10	3
25 min.					13	6	12	10	9	4	8	3
30 min.	—	—	—	—	11	5	10	10	5	4	8	3
Grand Mean	8	15	12	20	14	5	9	13	5	4	7	3

(1) - Mean of samples taken at two heights in enclosure.
(2) - After completion of discharge.

Source: Reference 8

of where it should be of little concern. Fires large enough to produce substantial agent decomposition are in themselves a substantial hazard.

REFERENCES:

1. NFPA No. 12A-1971, Standard on Halogenated Fire Extinguishing Agent Systems - Halon 1301, National Fire Protection Association, Boston, Mass.

2. C. L. Ford, "Halon 1301 Surface-Fire Extinguishment Data," Memorandum to NFPA Committee on Halogenated Extinguishing Agent Systems, November 21, 1967.

3. J. A. Floria, "Marine Diesel Oil - Determination of Extinguishing and Inerting Concentrations with 'Freon' FE 1301," du Pont "Freon" Products Laboratory Technical Report KSS-7026, 1970.

4. C. L. Ford, "Extinguishment of Deep-Seated Fires with Halon 1301," Memorandum to NFPA Committee on Halogenated Extinguishing Agent Systems, November 22, 1967.

5. J. A. Floria, "Determination of Hydrogen Fluoride and Hydrogen Bromide Concentrations Generated During Extinguishment of Class B Fires by Varying the 'Freon' FE 1301 Extinguishing Agent Discharge Rate," du Pont "Freon" Products Laboratory Technical Report KSS-6405, November 11, 1968.

6. J. A. Floria, "Quantitative Determination of Pyrolysis Products Produced by Varying the 'Freon' FE 1301 Fire Extinguishing Agent Discharge Rates During Extinguishment of n-Pentane Fires," du Pont "Freon" Products Laboratory Technical Report KSS-6801, December 29, 1969.

7. J. A. Floria, "Quantitative Determination of 'Freon' 1301 Pyrolysis Products Produced During the Extinguishment of Large-Scale n-Heptane Fires," du Pont "Freon" Products Laboratory Technical Report KSS-7054, January 4, 1971.

8. "Halon 1301 Computer Fire Test Program - Interim Report," Insul, Cardox, du Pont, Fenwal, January 10, 1972.

9. E. C. Creitz, "Inhibition of Diffusion Flames by Methyl Bromide and Trifluoromethyl Bromide Applied to the Fuel and Oxygen Sides of the Reaction Zone," J. Res. of Nat'l. Bur Stds., 65, No. 4, 1961.

10. H. E. Phillips, "Inerting Ethylene/Air Mixtures with 'Freon' FE 1301," du Pont "Freon" Products Laboratory Technical Report KSS-5577, 1966.

11. D M. Lundquist, "Evaluation of 'Freon' FE 1301 Mixtures as Fire Extinguishing Agents," du Pont "Freon" Products Laboratory Technical Report KSS-4687, 1964.

12. J. Miller, "Evaluation of the Fire Extinguishing Characteristics of 'Freon' FE 1301 on Flammable Liquid Fires," Factory Mutual Research Corporation, Serial No. 16234.1, 1967.

13. F. G. Kamowski, "Comparative Total Flooding Tests, Carbon Dioxide, and Bromotrifluoromethane," Fyr-Fyter Company Project No. 245, 1964.

14. D. M. Lundquist, "'Freon' FE 1301 Total Flooding Extinguishment System," du Pont "Freon" Products Laboratory Technical Report No. KSS-4620, 1964.

15. D. L. Ellis, "Fire Extinguisher System Test," Douglas Aircraft Company, Report No. DAC-33900, 1967.

16. M. J. Miller and R. L. Pote, "Fire Tests of Two Remote Area Fire Suppression Systems Concepts," Factory Mutual Research Corporation, Serial No. 15974.1, November 29, 1965.

17. M. J. Miller, "Extinguishment of Charcoal, Wood, and Paper Fires by Total Flooding with 'Freon' FE 130/Air and Carbon Dioxide/Air Mixtures," Factory Mutual Research Corporation, Serial No. 16234.1, July 28, 1967.

18. W. Haessler, Fyr-Fyter Company Interoffice Memorandum dated November 24, 1964.

19. J. A. Floria, "Determination of Volume Percentage 'Freon' FE 1301 Required to Inert Air at One Atmosphere Total Pressure Using Open Cell Polyurethane Foam as the Fuel," du Pont "Freon" Products Division Technical Report KSS-6674, September 3, 1969.

20. R. Cholin, "How Deep is Deep?" Talk presented to National Fire Protection Association Annual Meeting, San Francisco, May 18, 1971.

21. W. M. Gawin, (Underwriters' Laboratories, Inc.) Communication to NFPA Committee on Halogenated Extinguishing Agent Systems, August 17, 1971.

REMARKS

Dr. Walter: The next presentation will be by Julius J. Gassmann of FAA-NAFEC. He will talk about the "Application of Halon 1301 to Aircraft Cabin and Cargo Fires." One of the co-authors of this is John Marcy.

APPLICATION OF HALON 1301 TO AIRCRAFT CABIN AND CARGO FIRES

Julius J. Gassmann and John F. Marcy

Federal Aviation Administration

INTRODUCTION

Over the past 20 years the aviation industry has had considerable experience in the development and use of halogenated extinguishing systems for the protection of aircraft against fires occurring within the engine nacelle. The reason for this concern over fire safety was that this type of fire was considered as perhaps the most severe likely to occur in flight. However, this experience with the extinguishing systems utilizing Halon 1301 agent (Bromotrifluoromethane - CF_3Br) until recent years has been mostly confined to the control of fires involving the ignition and burning of flammable fluids rather than solid combustible materials as is the case with Class A fires.

Indeed Federal Regulations have required for the past 10 to 15 years or since about the beginning of the jet age in air transport that Halon 1301 systems be installed in commercial transport to control engine fires. In contrast, the application of Halon 1301 as an extinguishing agent for Class A fires in aviation involving fires in cabin materials and cargo has evolved slowly in spite of numerous studies and tests conducted to appraise the effectiveness and hazards of this chemical as demonstrated by the scope and attendance of this symposium. The reasons for this lag in the introduction of Halon 1301 in aviation are numerous and varied. First, the extent and seriousness of the experience with Class A fires in aircraft, especially in flight have been so rare as to contribute only slightly to the overall safety hazards in aviation. Based on this low estimation of fire risks balanced against costs of the system and especially the severe penalty of its weight, fire extinguishment was considered impractical. Instead, to improve cabin fire protection much emphasis during the past five years was placed on raising the flammability requirements of the cabin materials to limit the spread of fire. Regulations since 1947 have restricted the use of interior materials to those designated as "flame resistant" showing a slow burn rate of four inches per minute or less. Since 1967 new standards have been adopted so that at present nearly all materials being used in the latest air transport are required to be self-extinguishing within a six- or eight-inch burn length as determined by a prescribed test method according to the use of the particular material in the cabin. The risk of rapid and extensive spread of flames, especially from a small ignition should be greatly diminished with the use of new materials, capable of meeting the latest requirements of FAA Notice for Proposed Rule Making - NPRM 69-33

However, as the size of the latest transport airplanes and the number of passengers carried aboard continues to increase, it becomes necessary to consider new concepts for reducing still further the possible fire hazards.

In this respect, aviation has long been considered the leader and innovator in fire technology and safety. Also, aviation is in a favorable position to benefit from the increasing interest in the fire problem that has become a national issue since the enactment and recent extension of the Flammable Fabrics Act Amend PL 90-189 of 1967 and Fire Research and Safety Act, PL 90-259 of 1968. This as well as other activities by government agencies and technical groups should greatly accelerate the progress toward greater fire safety in all areas.

The main stumbling block to the use of Halon 1301 to protect habitable areas from fire has been the fear of exposing passengers to the breathing of both the gaseous agent and in particular its very toxic decomposition gaseous byproducts. Numerous investigations have been conducted to minimize this hazard by determining the conditions for its safe use in combating fire.

Portable Halon 1301 units designed for the fire protection of cabins while the airplane is undergoing maintenance in the hangar have been available for several years. The Aviation Committee of the National Fire Protection Association (NFPA) has recently drafted a document of recommended practices for the use of such systems which specify minimum concentrations of Halon 1301 (three to six percent) to extinguish the fire, maximum concentrations (ten percent) for safe breathing and maximum preburn times (ten seconds) to limit pyrolysis of the agent by fire.

At present, FAA at its test facility in Atlantic City is preparing a completely furnished DC-7 airplane cabin for tests utilizing a prototype permanently installed Halon 1301 system designed for in-flight operation. The test program to be completed over a period of two years or more will consider optimum design systems to provide uniform distribution of Halon 1301 gas at any point inside the cabin. The effect of ventilation, exit and door openings on distribution and losses of the agent from the cabin will be measured simultaneously at 12 sampling points by a special fast response porous-plug type gas analyzer. Other effects pertaining to the compatibility of a rapid discharge Halon 1301 system with the safety of passengers will also be studied in finalizing the design for aircraft.

Work involving protection against fires in non-inhabited areas, such as cargo compartments, dates back to the mid 1940's. This was carried out at the Civil Aeronautics Authority (CAA) test facilities located in Indianapolis, Indiana, and concerned itself primarily with detection. Reasons for this were first, because extinguishing agents eliminated only the visible flames and had little effect on the smoldering fires and secondly, because the history of fires in cargo compartments indicated that incidents of fire were very infrequent. Furthermore, during these early years the compartments were relatively small and since fires in such compartments, when ventilation was limited, were

not considered a serious threat to safety, the added weight of any extinguishing system was not considered practical.

In recent years after it was realized that Halon 1301 was effective in combating fires in very low concentrations (i.e., five percent by volume) and cargo compartment volumes were increased manyfold, it was considered worthwhile to resume the work on cargo compartment fire extinguishment. Hence, the project conducted in the Lockheed C-130 fuselage at the FAA facilities in Atlantic City, New Jersey, was initiated.

PART I - CABIN MOCKUP FIRES

Test Procedures

Fire extinguishing tests utilizing Halon 1301 were conducted on urethane seat foam and wool drapery ignited inside a closed 640-ft^3 insulated enclosure simulating the airplane cabin mockup. A description of tests and results of the findings are contained with other fire studies in FAA Report No. FAA-RD-70-81, titled, Air Transport Cabin Mockup Fire Experiments.

A plan drawing of the mockup with the locations of the Halon 1301 aspirator discharge nozzle, fire load consisting of two three-foot square and four-inch thick flexible urethane pads weighing about ten pounds, thermocouples, smoke and gas sampling points, etc. is presented in Figure 1.

Temperatures were measured at 24 different points in the air and on surfaces throughout the interior of the cabin. Smoke density in percent obscuration of a beam of light through an optical path of one foot was measured at two locations. Concentrations of oxygen, carbon monoxide and carbon dioxide were measured continuously at two locations, one near the ceiling and the other at a lower height near the exit sign. A total heat flux transducer was used to measure radiant and convective heat on the opposite far side of the cabin wall. Colorimetric tubes placed inside the trailer at mid height above the floor and six inches from the wall near the exit sign were used to measure the concentrations of HF, HBr, Br_2/Cl_2, HCl, HCN and $COCl_2$.

The foam pads (ten pounds fuel load) were in most cases ignited from below by a propane-fed Bunsen burner flame of about three inches in height. In a few tests, an incandescent hot body (i.e. barbecue calrod) and chemicals consisting of about three ounces of hexamethylenamine and potassium chlorate and primed with gun powder were used in an attempt to ignite the foam.

Summary of Test Results

The effectiveness of Halon 1301 as a safe means for securing fire control within an enclosure is shown by the test results presented in

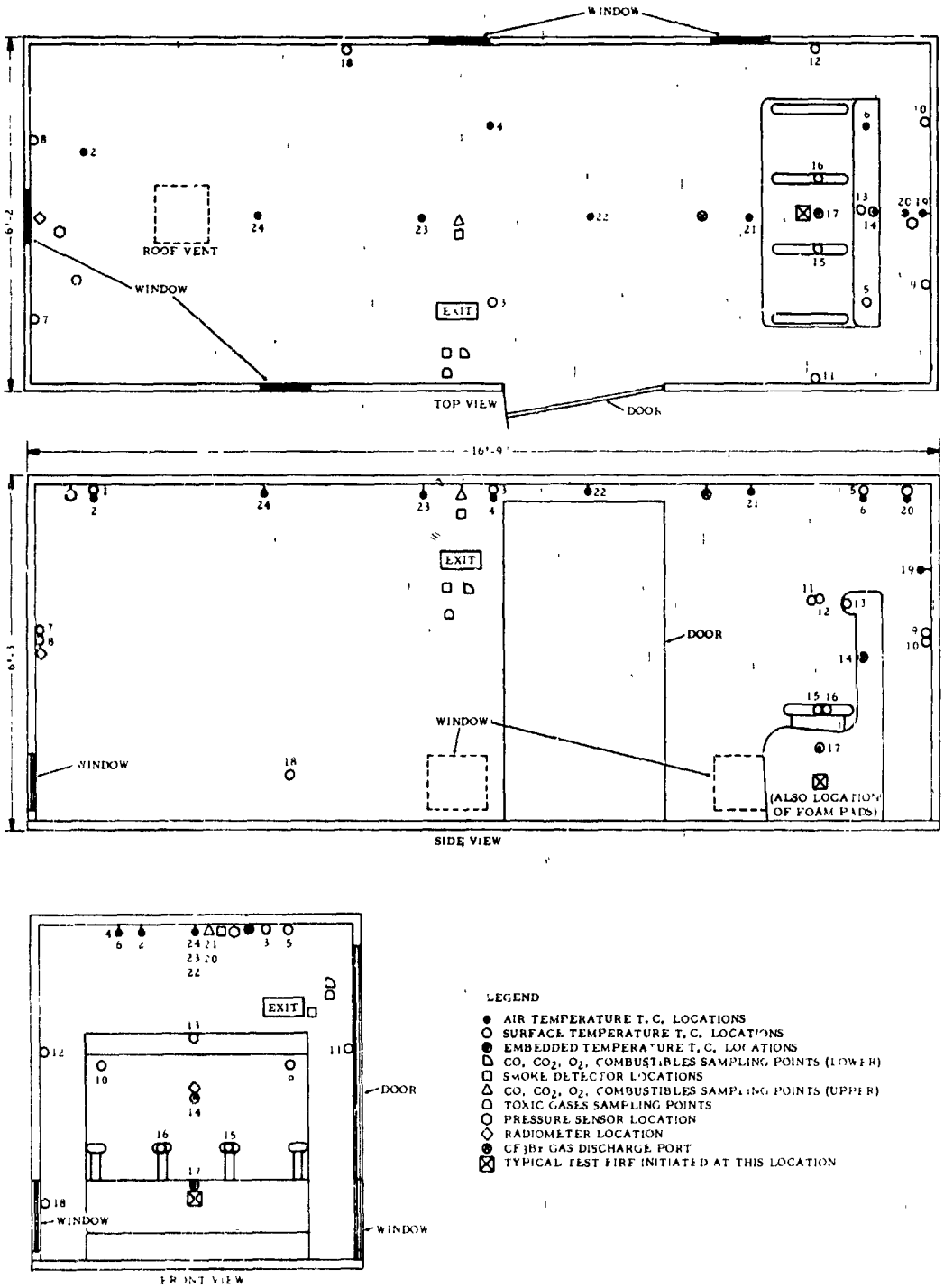


FIGURE 1. Cabin mockup schematic and instrumentation.

Table 1. In these tests the extinguishing agent was employed in different ways and amounts; namely, (1) low and high concentrations of about 3.5 to 7.0 percent by volume in air; (2) low- and high-rate discharges,

TABLE 1

Data Summary of Cabin Mockup Fire Tests

Test No	Type of Fire Test	Environment	Fuel Load	Ignition Source Type	Ignition Source Time (min)	Ceiling Temp. (°F)	Temp. (Max.) (°F)	Smoke Density (Max.) (%)	Oxygen (Min.) (%)	Carbon Monoxide (Max.) (%)	Combustibles (Max.) (%)	Radiant Heat (Max.) Btu/ft^2-s	Other Toxic Gases (ppm)	Remarks
1	Passenger Seat	Closed Cabin	Triple Seat with Conventional Materials (wool)	Propane/Air Burner	0.5	1070	1600	100	1.0	+1.5 0.5%/26.0 min 1.0%/26.5 min	N.D.(2)	N.D.(2)	HCL-150 HCN-10 NH_3-20 NO_2-0 Cl_2-8 $COCl_2$-1	Flash-fire at 25.5 min. No appreciable rise in temp. for 22 min.
2	Passenger Seat	Closed Cabin	Triple Seat with Conventional Materials (nylon)	Propane/Air Burner	1.0	1050	1970	100 50%/5.3 min 85%/10.0 min	1.8	+1.5 0.5%/12.8 min 1.0%/13.1 min	3.3	2.1		Flash-fire at 12.5 min. Exit sign partially legible in 50% smoke and obliterated in 85% smoke. Weight loss of seat 3.1 lb.
3	Passenger Seat	Vented Cabin—1 Ft^2 Roof Vent	Triple Seat with Conventional Materials (nylon)	Propane/Air Burner	1.0	1270	+2000	100 50%/14.3 min 85%/16.1 min	3.0	+1.5 0.5%/16.5 min 1.0%/16.8 min	2.1	1.7		Flash-fires first at 16 min second at 22.5 min. +2000°F backwall near vent. Extensive destruction of seat and wall lining.
4	Urethane Seat Foam	Closed Cabin	Regular Urethane Foam Approx. 10 lb	Propane/Air Burner	0.5	1420	+2000	100 50%/1.9 min 85%/2.2 min	2.5	+1.5 0.5%/3.1 min 1.0%/3.3 min	2.4	2.9		Flash-fire at 2.6 min. Reignition of foam after door opened in 12.0 min. Lazy type low intensity flames seen near floor after door closed for 13 min. All foam consumed.
5	Extinguishment - Slow Discharge of Agent 1301 During Early Stage of Fire	Inerted Cabin—10.7 lb CF_3Br (4.1% by V)	Regular Urethane Foam Approx. 10 lb	Propane/Air Burner	1.0 Sporadic(3) (5 min)	100	150	58 58%/6.0 min	20.6	0.1	0.2	<0.10	HF>15 Br_2-0.5	Flash-fire prevented by gas discharge after 3.1 min. Destruction of foam less than 10%.
6	Extinguishment - Slow Rate Agent 1301 Discharge Just Prior to Anticipated Flash-Fire	Inerted Cabin—9.8 lb CF_3Br (3.6% by V)	Regular Urethane Foam Approx. 10 lb	Propane/Air Burner	1.0 Sporadic (5 min)	330	1580	100 50%/3.1 min 85%/3.4 min	16.7	1.1	0.6	0.35	HCL-75 HF-8 Br_2-5 $COCl_2$-0.8	Flash-fire prevented by gas discharge after 3.5 min. Propane burner operation erratic. Will not continue to maintain flames when spark ignited.
7	Extinguishment - Slow Rate Agent 1301 Discharge Before and After Ignition	Inerted Cabin—9.2 lb CF_3Br Bottle No. 1 9.1 lb Agent Bottle No. 2 Total 18.3 lb (7.2% by V)	Regular Urethane Foam Approx. 10 lb	Propane/Air Burner Chemicals Incandescent Calrod (500w)	Sporadic (7.5 min) 1 6	250	260	99 50%/12.2 min 85%/15.0 min	20.0 19.2	0.45	0.1 0.7	<0.05 <0.05	HCL-100 Br_2>50 $COCl_2$-1.5	No flash-fire or flaming of the foam observed. Burner will not ignite in 7.1% by V gas atm. Foam charred by heated calrod but did not flame. Foam burst into flame and burned completely after door was opened. Very pungent bromide odor
8	Extinguishment - Slow Rate Agent 1301 Discharge Before Ignition	Inerted Cabin—10.1 lb CF_3Br (3.9% by V)	Wool Drapery	Propane/Air Burner Chemicals Incandescent Calrod (500w)	Sporadic (5.5 min) 1 5	150	200	38	20.0	0.09	0.1	<0.05		Drapery fire prevented. No open flaming of the fabric. Chemicals burned intensely with high flames for 1 to 1.5 min until consumed. Fabric charred by heat - 12% by W.

Test No	Type of Fire Test	Environment	Fuel Load	Ignition Source Type	Ignition Source Time (min)	Ceiling Temp. (°F)	Temp. (Max.) (°F)	Smoke Density (Max.) (%)	Oxygen (Min.) (%)	Carbon Monoxide (Max.) (%)	Combustibles (Max.) (%)	Radiant Heat (Max.) Btu/ft^2-s	Other Toxic Gases (ppm)	Remarks
9	Extinguishment - High Rate Agent 1301 Discharge (10 sec) When Ceiling Temperature Reached 200°F	Inerted Cabin - 14.1 lb CF3Br (5.8% by V)	Regular Urethane Foam - Approx. - 10 lb	Propane/Air Burner	1.0 Sporadic (4 min)	180	220	60 50%/4.0 min	19.4	0.06	0.13	<0.05		No flash-fire. Flaming of foam pad rapidly extinguished. Chemicals and calrod did not cause open flaming. Destruction of foam only 12% by W.
				Chemicals	1									
				Incandescent Calrod (2000 W)	10			78	19.0	0.18	0.25	< 0.05		Bromide odor much less noticeable than above.
10	Flame-Retardant (FR) Urethane Seat Foam	Closed Cabin	FR Urethane Foam - Approx. - 11 lb	Propane/Air Burner	12	120	130	65 50%/5.9 min	20.0	< 0.1	< 0.1	< 0.05	HCL-2 Br_2-0.5 $COCl_2$-0.5	No flash-fire or appreciable rise in cabin temp. Destruction of foam less than 10% by W. Burning of foam only in direct contact with propane flames. Heavy white smoke in 4.0 min.
11	Flame-Retardant (FR) Urethane Seat Foam	Closed Cabin	FR Urethane Foam - Approx. - 11 lb	Chemicals	1	250	280	96 50%/1.1 min	20.5	0.6	0.5	< 0.05		Chemical fire ignited foam causing open flaming for 1.7 min after chemicals consumed.
				Incandescent Calrod (2000 W)	3.8	560	1650	100 50%/1.7 min	20.0	0.7	0.6	0.25		Incandescent calrod caused flash-fire in 4 min. Destruction of foam about 50% by W.
12	Flame-Retardant (FR) Urethane Seat Foam	Closed Cabin	FR Urethane Foam - Approx. - 11 lb	Kerosene Pan Fire - 8 oz	3	300	410	100 50%/0.7 min 85%/0.9 min	18.7	0.37	0.5	0.07		No flash-fire or evidence of self-flaming of foam. Complete obliteration of Exit sign in 0.9 min. Destruction of foam less than 10% by W.
13	Flame-Retardant (FR) Urethane Seat Foam	Vented Cabin - 1 ft^2 Roof Vent	FR Urethane Foam - Approx. - 11 lb	Kerosene Pan Fire - 8 oz	3	280	350	100 50%/0.9 min 85%/1.3 min	19.3	0.23	0.3	0.07		No flash-fire. Fire growth and smoke build-up similar to closed cabin test (No. 12). Exit sign completely obliterated in 1.1 min.
14	Urethane Seat Foam Fire Outdoors	Free Burning	Regular Urethane Foam - Approx. - 10 lb	Kerosene Pan Fire - 1 oz	2	No Measurements								Regular urethane foam completely consumed in 6.0 min.
			FR Urethane Foam - Approx. - 11 lb	Kerosene Pan Fire-10 oz	6									FR urethane foam flames out in 2.7 min although fire burned about 10 min. Foam only consumed directly above kerosene fire.
15	Interior Materials - Initiated By Foam Flash Fire	Closed Cabin	Regular Urethane Foam - Approx. 5 lb	Propane/Air Burner	1.0	480	525	100 50%/2.9 min 85%/4.1 min	15.0	0.29	0.4	0.25		Interior materials slightly damaged but still serviceable. No flash-fire of foam as expected. High humidity conditions.
16	Interior Materials - Initiated By Foam Flash-Fire	Closed Cabin	Regular Urethane Foam - Approx. - 10 lb	Propane/Air Burner	0.5	1440	1440	100 50%/7.4 min 85%/8.2 min	4.4	+1.5	1.9	1.0		Interior materials extensively damaged by flash-fire. Temp. range of 1000°F to 1500°F sustained for approx. 1 min. Even the heaviest materials tested were totally charred.
17	Curtain Divider Effect On Fire Spread	Closed Cabin - Asbestos Curtain 37 in Length Suspended From Mid-Ceiling	Regular Urethane Foam - Approx. - 10 lb, Strips of Interior Materials Also Suspended From Ceiling	Propane/Air Burner	0.5	1570	1570	100 50%/5.9 min 85%/6.5 min	3.2	+1.5	2.1	0.6		Ceiling temp. directly behind curtain 600°F lower than in front towards fire. Initial smoke buildup behind curtain delayed 1.5 min. Suspended materials protected behind curtain showed less fire damage than in front.
18	Neoprene Foam Fire Outdoors (4 Types)	Free Burning	Neoprene Foam - Approx. - 12.5 lb	Kerosene Pan Fire - 10 oz	4	No Measurements								No flash-fire. Improved FR neoprene foam burned with no appreciable self-flaming but with heavy smoke. Foam continued to smolder until totally reduced to char after several hrs.
19	Neoprene Foam Fire Outdoors (Improved Type)	Free Burning	Neoprene Foam - Approx - 12 lb	Kerosene Pan Fire - 10 oz	3	No Measurements								Fire out in 2.3 min. Foam did not appear to self-flame. Foam charred only to a depth of 1 in. No fire penetration of foam pad.

Test No.	Type of Fire Test	Environment	Fuel Load	Ignition Source Type	Ignition Source Time (min)	Ceiling Temp. (°F)	Temp. (Max.) (°F)	Smoke Density (Max.) (%)	Oxygen (Min.) (%)	Carbon Monoxide (Max.) (%)	Combustibles (Max.) (1)	Radiant Heat (Max.) Btu/ft-^{2}s	Other Toxic Gases	Remarks
20	Curtain Divider Effect Onfire Spread	Closed Cabin	Regular Urethane Foam - Approx. - 10 lb	Propane/Air Burner	0.5	950	1400	97 50%/10.7 min	5.0	1.3	1.5	0.5		Materials suspended over fire exposed to temp. of 1200°F to 1400°F for 1 min completely destroyed. Materials suspended at opposite end of fire exposed to 600°F to 700°F for 1 min. only minor damage.
21	Curtain Divider Effect Onfire Spread	Closed Cabin - Asbestos Curtain 12 in - Length Suspended From Mid-Ceiling	Regular Urethane Foam - Approx. - 10 lb	Propane/Air Burner	1.0	980	1480	98 50%/9.8 min 85%/11.1 min	4.0	1.1	1.0	0.9		Materials suspended behind curtain exposed to temp. of 800°F to 1000°F partially charred. Materials located at far end from fire exposed to 600°F to 800°F only partially melted and blistered.
22A	Neoprene Seat Foam (Improved Type)	Closed Cabin	Neoprene Foam - Approx. - 14 lb	Alcohol Pan Fire-20 oz	8	230	240	94 50%/3.4 min	18.3	0.21	0.3	<0.05		No flash-fire by either alcohol flames or incandescent calrod.
22B	Neoprene Seat Foam (Improved Type)	Closed Cabin	Neoprene Foam - Approx. - 14 lb	Incandescent Calrod (2000 W)	10	100	100	72 50%/12.4 min	20.5	0.01	< 0.5	<0.05		Slow buildup of smoke and CO. Odor not offensive as with urethane. Slow and total destruction of foam by char formation after several hours outdoors.
23	Window Opening Effect On Urethane Foam Fire	Vented Cabin - 4 ft^2 Opening	Regular Urethane Foam - Approx. - 10 lb	Propane/Air Burner	1.0	1360	1610	99 50%/8.3 min 85%/11.3 min	6.4	+1.5	1.8	1.6		Flash-fire and smoke buildup not appreciably affected by opening. Foam completely consumed in 28 min.
24	Window Opening Effect On Urethane Foam Fire	Vented Cabin - 9 ft^2 Opening	Regular Urethane Foam - Approx. - 10 lb	Propane/Air Burner	1.0	1650	2140	100 50%/8.0 min 85%/8.9 min	0.5	+1.5	3.8	1.5		Very severe flash-fire with destruction of cabin lining. Oxygen depletion surprisingly high with rapid recovery to 16% in 1 min. Foam completely consumed in 20 min. Large flames extending out of opening.
25	Window Opening Effect On Urethane Foam Fire	Vented Cabin - 9 ft^2 Opening	FR Urethane Foam - Approx. - 11 lb	Kerosene Pan Fire-8 oz	3	1580	1810	100 50%/1.3 min 85%/1.5 min	3.0	1.4	N.A.	0.9		Flash-fire unexpected with FR foam. Large flames extending out of opening. Note * No flash-fire in similar tests with closed cabin as in Tests 10, 12, and 13.
26	Door Opening Effect On Urethane Foam Fire	Vented Cabin - 18 ft^2 Opening	FR Urethane Foam - Approx. - 11 lb	Kerosene Pan Fire-8 oz	3	1800	+2200	100 50%/1.9 min 85%/2.2 min	2.0	+1.5	N.A.	1.3		Very severe flash-fire unexpected. Foam melted and burned on the floor. Very high temperatures obtained.
27	Kerosene	Closed Cabin	No Other Fuel Load	Kerosene Pan Fire-8 oz	3	330	360	80 50%/1.6 min	17.5	0.03	N.A.	< 0.05		No flash-fire. Only gradual increase in temp. Exit sign still visible but not legible.
28A	Passenger Seat	Closed Cabin	Triple Seat With Improved Materials (S.E. (4) Type)	Propane/Air Burner - 10 in Flames	15	90	100	41	21.0	0.02	N.A	<0.05		No flash-fire. Seat fabrics and foam burned only in area of 10-in. propane flames. No appreciable change in ambient conditions.
28B	Passenger Seat	Closed Cabin	Triple Seat With Improved Materials (S.E. Type)	Kerosene Pan Fire-8 oz	3	450	610	100 50%/1.3 min 85%/1.7 min	16.0	0.45	N.A	0.20		No flash-fire as in previous seat tests. Fire damage only to center seat directly above kerosene fire. Extensive damage to center bottom bad. Very heavy smoke in 1 min. almost obscured Exit sign. Re-ignition of foam pad and open flaming after door opened in 10 min. Heavy gray choking smoke.

NOTES
(1) Data in terms of CO percent heating value.
(2) N.A. meaning no data taken.
(3) Discharge of CF_3Br gas extinguished propane/air burner flames. However, gas burner could be reignited sporadically in CF_3Br by continuous electrical sparking.
(4) S.E. meaning self-extinguishing.

and (3) discharge before, during and after the fire to check for possible reignition of fire. The usefulness of the agent was also evaluated for different types of ignition sources; namely, (1) propane/air mixture; (2) incandescent heat; and (3) chemicals containing their own oxygen supply. Also, extinguishing tests were conducted on both smoldering and open flaming urethane fires.

For Tests Nos. 5 through 8, Halon 1301 agent was discharged by opening the valve of a standard compressed cylinder. The discharge was relatively slow and occurred at a diminishing rate requiring about two minutes to be completed.

In Test No. 5, Halon 1301 at a concentration in air calculated at 4.1 percent by volume was discharged one minute after ignition of the foam pad when flaming became self-sustaining. Flaming of the foam was extinguished within 1.5 minutes after the discharge of the agent. Although the propane/air mixture used by the burner was still flammable (although erratic when ignited by electrical sparking), the foam could not be made to burn with an open flame. Foam consumed in this test was less than one pound.

In Test No. 6, Halon 1301 at 3.6 percent concentration was again discharged from a standard cylinder but at a later time when the ceiling temperature had approached 150°F and a flash fire appeared imminent from past experience as shown by the steep rise in the temperature curve and sharp drop in the oxygen content of the air as plotted in Figure 2. Although the ceiling temperature increased to 300°F following the slow discharge of the agent, a flash fire did not develop. The effectiveness of Halon 1301 is shown by a comparison of the curves presented in Figures 2 and 3. The same fire conditions were present in both Tests Nos. 4 and 6 except that no agent was used in Test No. 4. In the latter test, burning of the foam continued until a flash fire occurred. The fire parameters for Test No. 6, related to time and to each other, are presented in Figure 3 for comparison with Test No. 4. The same conditions were present in both tests except for the use of Halon 1301 to extinguish the fire.

In Test No. 7 Halon 1301 was discharged from two cylinders -- one during the fire as in the previous test and the other after the fire was extinguished. Total Halon 1301 discharged into the cabin was calculated at 7.1 percent concentration. At this higher concentration the propane/air mixture of the burner could not be ignited by electrical sparking as before. However, the chemicals were readily ignited and burst into flames which reached almost to the ceiling. Although of only short duration, a high heat source developed from the burning chemicals on top of pads, which failed to ignite the foam to a flame. An electrically-heated element (i.e., barbecue grill) with an output of 500 watts heat placed in direct contact with the foam also failed to cause flaming combustion. Considerable smoke was generated by the smoldering combustion.

In Test No. 8 a folded wool curtain 2-1/2 feet wide and 5 feet in height was suspended from the ceiling near the center of the mockup.

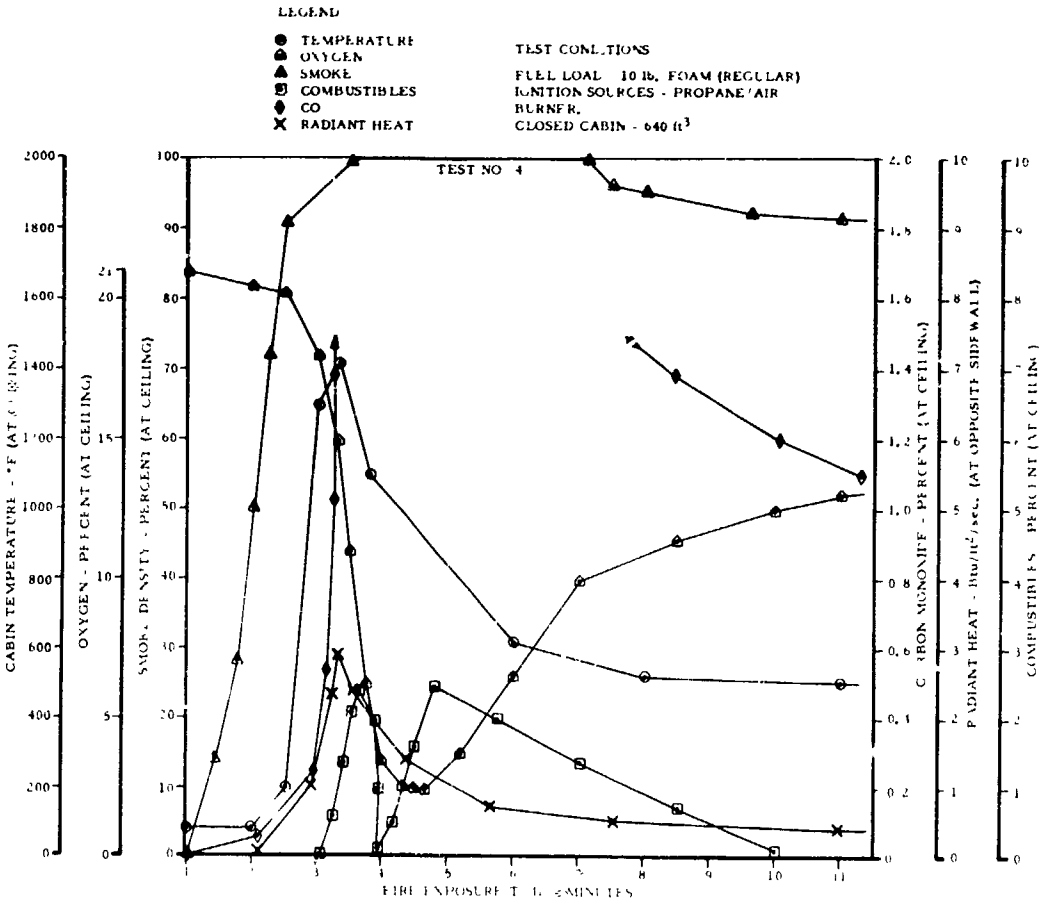


FIGURE 2. Regular urethane foam fire parameters in closed cabin.

The curtain from below was subjected to a propane/air flame, chemical fire as in the previous test and contact with the 500 watt incandescent element. A 3.9 percent Halon 1301 agent concentration was discharged into the mockup before attempts were made to ignite the fabric. No flaming combustion could be obtained with the three types of heat sources although considerable charring of the fabric resulted.

In Test No. 9 an aircraft type extinguishing system for engine fires was used for the rapid discharge of 14.1 pounds of Halon 1301 equivalent to a 5.8 percent concentration of the agent inside the mockup. Rapid discharge was effected by pressurizing the bottle with nitrogen to 600 psi and releasing the contents of the bottle by an explosive rupture of a disk to provide a large outlet. The fire parameters for this test related to time and each other are presented in Figure 4. Halon 1301 was discharged when the ceiling temperature approached 150°F and at a time when a flash fire was a threat. From visual observations and the curves, it was shown that the flames were extinguished within a few seconds. Neither the chemical fire as in the previous test or the incandescent element with a heat output of 2,000 watts could reignite the foam to a flaming combustion. Considerable smoke emission was produced by smoldering combustion as shown in Figure 4.

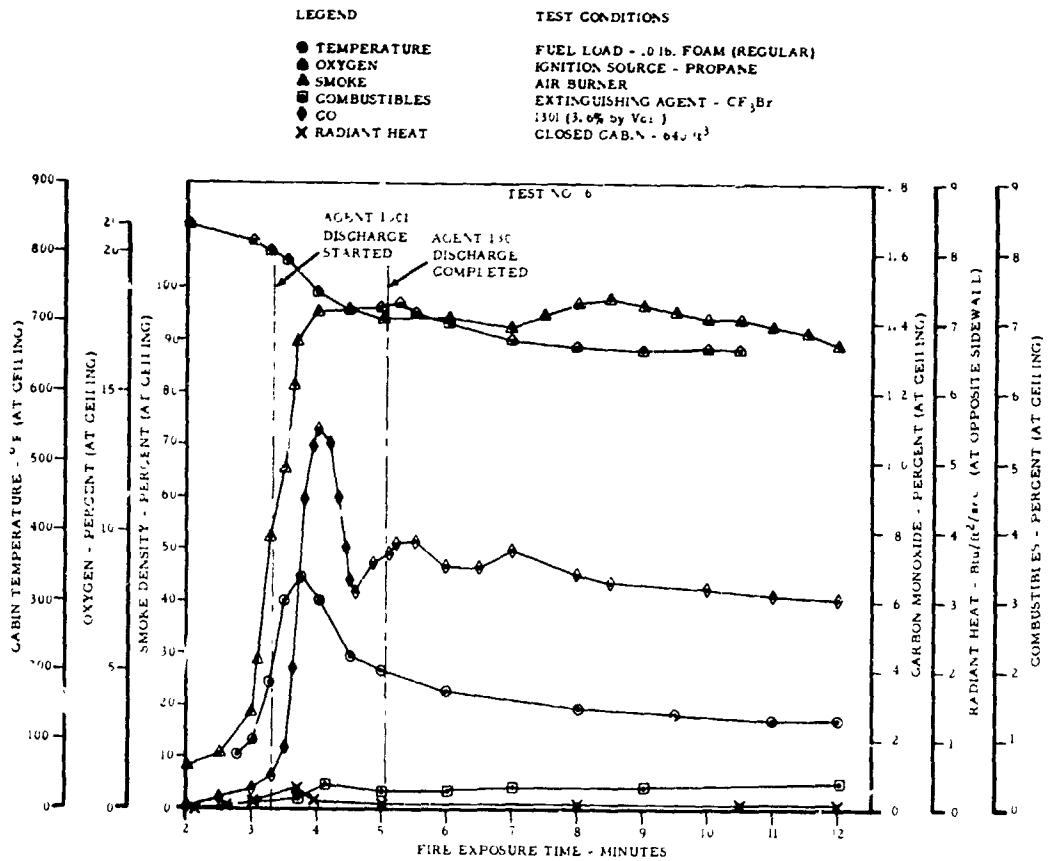


FIGURE 3. Urethane foam fire extinguishment parameters (slow rate agent discharge).

Data on toxic gases, other than carbon monoxide resulting from the pyrolysis of Halon 1301 subjected to fire is meager and inconclusive. Only a few general observations on the toxic hazards are possible from the available test data herein. This subject has been investigated much more thoroughly by the Bureau of Mines for the Air Force. In the tests, concentrations of HBr and HF, highly toxic gases resulting from the dissociation of Halon 1301 were measured as a function of preburn time of a cotton sheeting fuel load. Results of these tests are contained in Air Force Technical Report AFAPL-TR-70-39, titled, "Fire Suppression for Aerospace Vehicles," dated July, 1970.

Concentrations of toxic gases in parts per million (ppm) in air obtained with colorimetric tubes are given in Table 1. HF and Br_2 concentrations exceeding 15 and 50 ppm are, respectively, reported. Also, very obnoxious fumes with a bromide odor were experienced when the mock-up door was opened after extinguishment of the foam fire. This was especially noticeable for tests during which considerable pyrolysis of Halon 1301 was evident from the prolonged exposure of this agent to a large fire (i.e., long preburn time).

CONCLUSIONS

Based on an analysis of the results of a limited number of tests, it was determined that:

1. A high-rate discharge system utilizing Halon 1301 at a concentration of 5.8 percent in air is effective in rapidly extinguishing a Class A fire in urethane seat padding.

2. Prolonged exposure in a cabin fire to flames and heat from incandescent hot bodies can cause pyrolysis of Halon 1301 into extremely toxic gases in concentrations that may be harmful.

3. Although Halon 1301 concentrations as low as three to four percent in air were sufficient to extinguish Class A fires, the propane-gas burner could still be ignited to flame by electrical sparking. However, when the concentration was doubled the propane/air mixture at the burner was no longer flammable.

4. Halon 1301 may not be effective in the recommended range of five to ten percent concentrations when used on chemicals containing their own supplies of oxygen such as the chlorates.

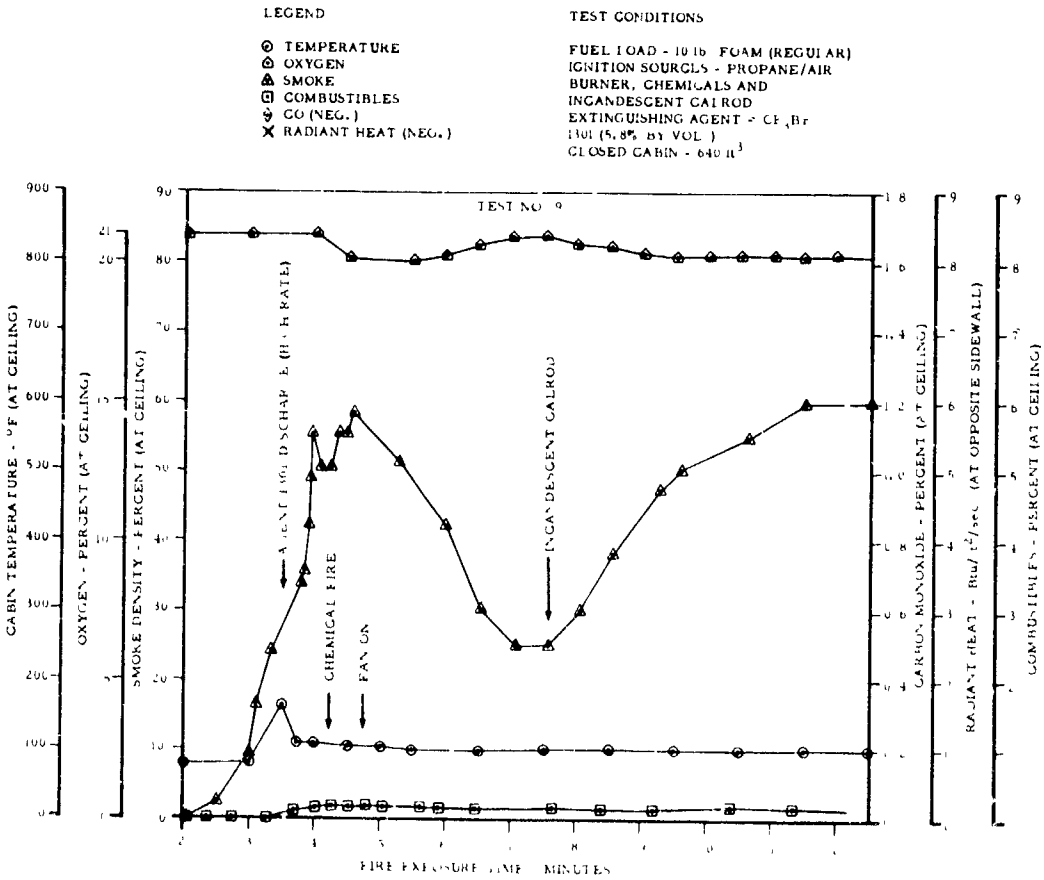


FIGURE 4. Urethane foam fire extinguishment parameters (high rate agent discharge).

PART II - CARGO COMPARTMENT FIRES

Test Procedure

The effectiveness of combating Class A fires using Halon 1301 as an extinguishing agent was demonstrated by conducting full-scale fire tests in a Lockheed C-130 fuselage section, that which lies between station 245 and 737. Aluminum bulkheads were fabricated and attached to the ends of the fuselage section. This provided a compartment with a volume of 5,000 cubic feet.

Two observation windows, each one foot square, were provided in each of the bulkheads. These were located just above the floor line. An air inlet, 14 inches in diameter, was located in the forward bulkhead five feet above the floor and a baffle was provided to reduce inlet air velocities and localized effects such as dead air spaces within the compartment. The 14-inch-diameter duct attached to the inlet contained an axial flow fan which was capable of moving air at the desired 2,000 cubic feet per minute, a set of straightener vanes, and a calibrated orifice for measuring the airflow. An air outlet was provided in the aft bulkhead. This outlet was 14 inches in diameter, fitted with a check damper for controlling airflow and located 1-1/2 feet from the top of the bulkhead. An aluminum flap was fabricated, to be interchangeable with the observation windows, to provide an outlet near the floor.

Throughout this program standard pieces of cargo were used both for the fire load and for the cargo load. This standard parcel consisted of a corrugated cardboard carton measuring 28 x 24 x 20 inches, weighing four pounds and filled with 16 pounds of excelsior. Thus each parced weighed a total of 20 pounds. Figure 5 shows a stack of 144 cargo-parcels and one open parcel on the scale showing its contents. This stack represents about one-half of the load used in the C-130 fuselage compartment when the 50-percent-load test was conducted.

Tests were conducted in the 5,000-cubic-foot C-130 fuselage compartment using a loading of ten percent by volume and a loading of 50 percent (for all practical purposes, nearly full). Two methods of extinguishment or fire control were used: (1) airflow shutoff; and (2) airflow shutoff plus bromotrifluoromethane (Halon 1301).

Four tests were run using airflow shutoff as a means of fire control. In these tests, as in all tests in this program, ignition was achieved by placing an electric barbecue lighter in the bottom center standard parcel of the fire load. Ignition (visible flames external to the cardboard container) usually occurred about three minutes after voltage was applied to the lighter. Twenty seconds after ignition, application of the voltage to the igniter was discontinued. During the ignition period and until detection occurred airflow through the compartment was maintained at 2,000 cubic-feet-per-minute or about one air change every 2.5 minutes. At the time of detection (when 300°F was recorded by any one of the thermocouples), the airflow was reduced to 75 cubic feet per hour.

FIGURE 5. Corrugated cardboard cartons containing excelsior.

Although temperatures at nine different locations were recorded, only the highest temperature trace was used in evaluating the data, because the lower temperatures were of less significance. The convection currents due to the heat generated by the fires had more effect on temperature distribution than the airflow through the compartment so the highest temperature, even before detection and airflow shutoff, invariably occurred at the thermocouples located above the fire location rather than downstream or at the air outlet. Therefore, only the highest temperature recorded was used to determine detection, fire severity, and for plotting the time-temperature curves.

In every cargo-fire extinguishing test conducted in this program, data were taken for two hours after the start of the tests. This permitted a determination to be made of the effectiveness of the control or extinguishing method employed in each particular test. At the end of this two-hour test period, since visual flames were extinguished but smoldering continued in every case, the fire was extinguished completely by introducing approximately 1,200 pounds of CO_2 from a Cardox system. The compartment was kept closed with zero airflow until the next day. With the possible exception of two occasions, the fire was out by then and after airing out the compartment for an additional day it could be emptied and cleaned in preparation for loading for the next test.

SUMMARY OF TEST RESULTS

In general the results of the tests conducted indicate that the relocating of the compartment outlet from the top to the bottom location

had no noticeable effect on the control afforded by either the airflow shutoff or the Freon 1301 extinguishant method for combating the compartment fire.

The results of a typical cargo-compartment fire test, ten-percent-load configuration, in which airflow shutoff was used to effect control are shown in Figure 6. In this test detection was assumed when a temperature of 300°F was indicated at which time the airflow was shut off. Shortly thereafter a flash fire occurred as evidenced by the rapid rise in pressure and temperature followed by a reduction in the percent oxygen reading which usually dropped to near zero percent and remained there for several minutes. During the flash fire a maximum temperature of 1,800°F and a pressure of 0.10 pound per square inch were recorded. In other similar tests temperatures of over 2,000°F and pressures up to 0.175 pound per square inch were recorded.

Results of the tests conducted using bromotrifluoromethane in addition to airflow shutoff (with simulated leakage) are shown in Figure 7. These results show that in all cases where an extinguishant is used in addition to airflow shutoff the flash fire was eliminated. They also indicated that both 100 pounds of agent (five percent by volume) and 60 pounds of agent (three percent by volume) were effective in extinguishing the flames and controlling the continuing smoldering condition for a two-hour period. The only noticeable difference between the three-

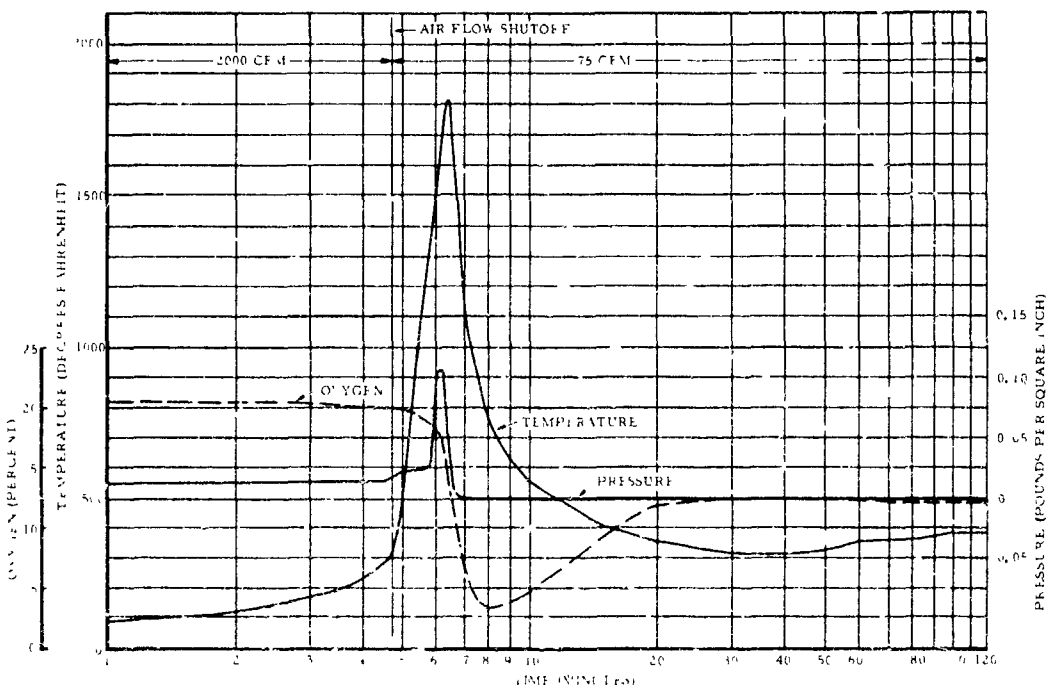


FIGURE 6. Temperature, pressure, and oxygen recordings of an airflow-shutoff fire-extinguishing test in the ten-percent-load configuration.

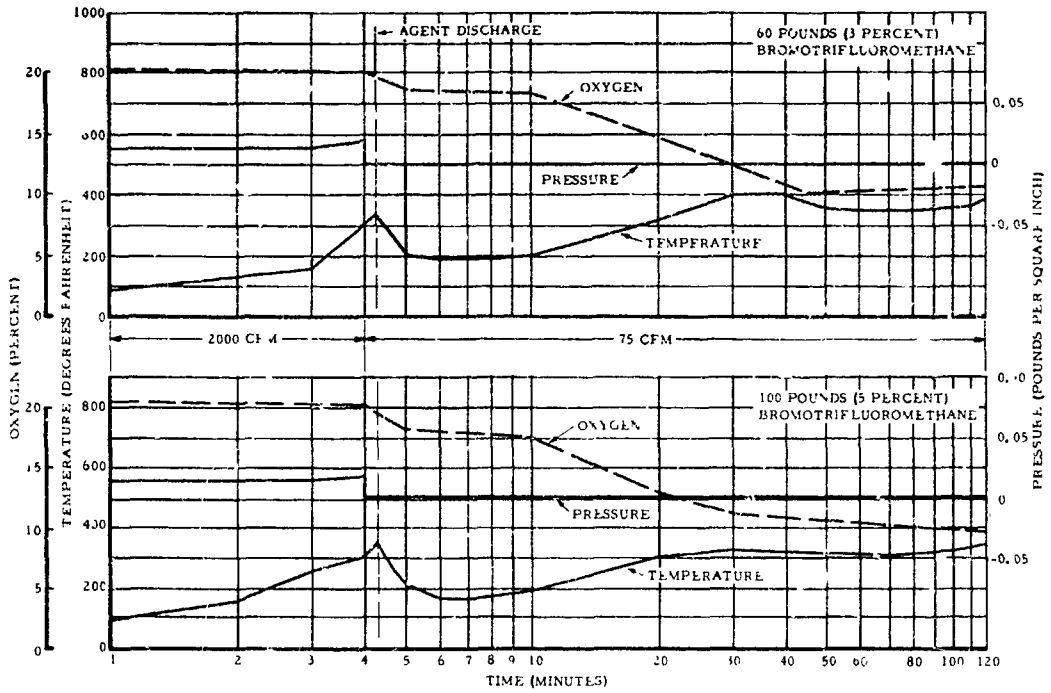


FIGURE 7. Temperature, pressure, and oxygen recordings of bromotrifluoromethane fire-extinguishing tests in the ten-percent-load configuration.

and-five-percent agent tests was that the compartment temperature, due to the smoldering cargo, remained between 50° and 100°F higher throughout the two-hour period when the lower agent concentration was used.

CONCLUSIONS

Based on the results of the tests conducted, it is concluded that in compartments with a volume of up to 10,000 cubic feet:

1. The use of bromotrifluoromethane extinguishing agent released at the time of detection of a cargo fire can prevent the occurrence of flash fire, greatly reduce the maximum temperatures, and provide effective fire control for periods of at least two hours.

2. The use of as little as three percent by volume of bromotrifluoromethane can effectively control cargo fires in a compartment with a ten-percent and a 50-percent load configuration.

REMARKS

Dr. Walter: Our next speaker is Lt. Col. Marshall Steinberg, U.S. Army Environmental Hygiene Agency, and he is going to describe the use of halogenated agents in a military vehicle.

TOXIC HAZARDS FROM EXTINGUISHING GASOLINE FIRES USING HALON 1301 EXTINGUISHERS IN ARMORED PERSONNEL CARRIERS

Marshall Steinberg

U.S. Army Environmental Hygiene Agency

ABSTRACT

The purpose of this study was to obtain information regarding the hazard to vehicle occupants associated with the use of an automatic fire suppression system using Halon 1301 in a gasoline fueled M113 Armored Personnel Carrier (APC). It is estimated that high concentrations of Halon 1301, gasoline, and HF present in the vehicle after fire suppression may cause signs of intoxication from inhalation of these compounds. It is the opinion of the author that the benefits of the Halon 1301 fire suppression system far exceed the risks.

The purpose of the study I would like to report on was to obtain information regarding the health hazards to vehicle occupants associated with the use of an Automatic Halon Fire Suppression System in gasoline fueled M113 Armored Personnel Carriers (APC). Data were collected in conjunction with cooperative tests conducted with the U.S. Army Test and Evaluation Command. The nature and degree of the toxic hazards were determined by evaluation of animal exposure data and by measurement of atmospheric contaminants created as a result of extinguishing gasoline fueled fires using Halon 1301 (bromotrifluoromethane).

The fires were initiated by firing a 3.5 inch high explosive anti-tank (HEAT) projectile through a vehicle's fuel tank. As a consequence of the perforation of the tank, a wire grid was ruptured. Rupture of the wire grid activated the Fire Suppression System and served as a basis for establishing time zero (t_o) in regard to the collection of data.

The fire was on the average suppressed by T_{+168} milliseconds (100-212 ms range). Atmospheric samples were collected from (Figure 1) inside the vehicle using 500 cc stainless steel cylinders evacuated to 50 microns of mercury. The essential components of the atmospheric collection system were placed in racks which were positioned in the vehicle as shown in Figure 2. With the exception of the first test when only one rack was used, these positions were applicable to all tests. Specific details regarding specimen collection are outlined in Figure 3.

Atmospheric samples were obtained from tests 1, 3, 4, 6 and 9. The electrical timing equipment for various reasons malfunctioned in

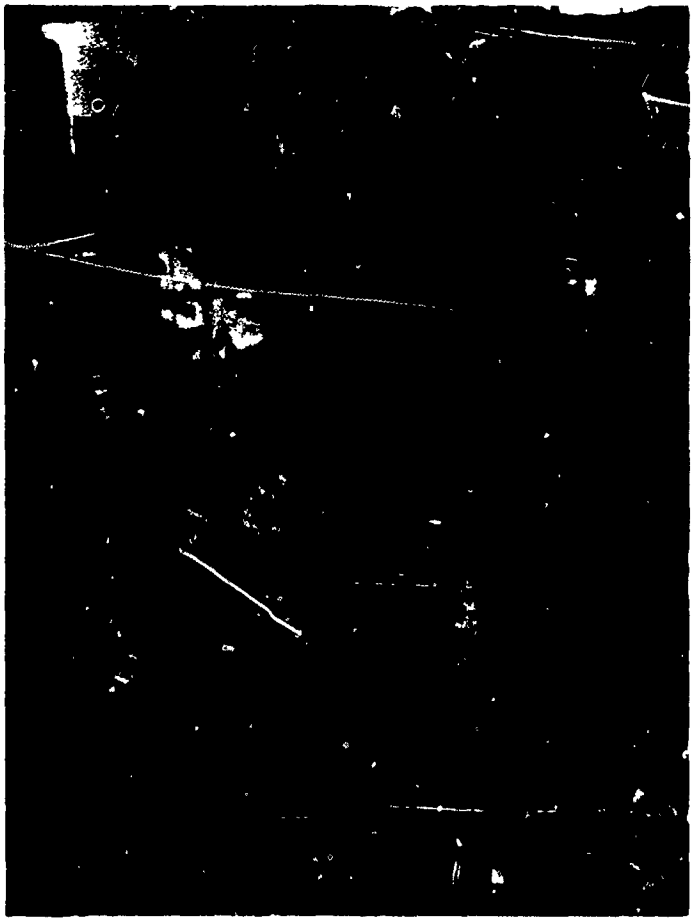


FIGURE 1.

2, 5, 7 and 8 preventing complete collection of sequentially programmed samples. In those tests wherein the fire was automatically suppressed, gas volumes were not corrected for temperature and pressure changes though recorded at the time of sample collection, because it was considered that the transient nature of these changes precluded their having a significant effect upon gas volumes.

In tests numbered 3, 4, 5 and 8, pigs were placed inside the M113 vehicle by the Biophysics Division, Biomedical Laboratory, Edgewood Arsenal, Maryland, in order to help estimate the potential hazard to vehicle occupants.

Atmospheric samples were analyzed for Halon 1301, gasoline, carbon monoxide and oxygen using a gas chromatograph. Fluoride ion (F^-) concentration was measured using a specific fluoride ion electrode. The concentration of fluoride ion in this report is expressed as parts per million of hydrogen fluoride.

The mean concentration of oxygen and carbon monoxide in preignition samples collected 60 seconds prior to the penetration of the HEAT round, was 20.6 and 0.0 percent by volume respectively. If one measures to only one place after the decimal point, the concentrations of oxygen and carbon monoxide following the activation of the fire suppression system were not significantly different from background levels.

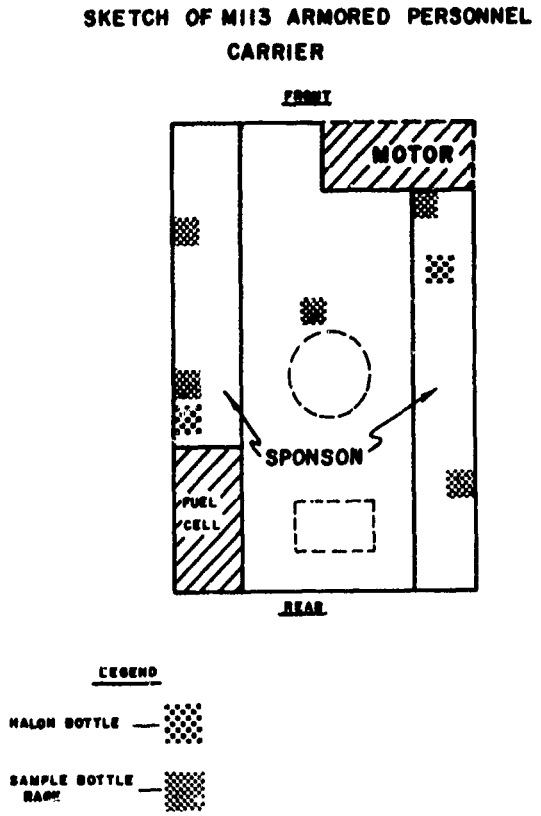


FIGURE 2. Sketch of M113 Armored Personnel Carrier.

The mean background fluoride ion concentration was 27 ppm by volume expressed as hydrogen fluoride (HF). This level was largely owing to test methodology and was not indicative of the atmosphere. This background was subtracted from all post ignition fluoride measurements (Figure 4).

The rapid decrease in the high concentrations of fluoride ion found in samples collected one second post ignition is evident. Although the mean concentration of fluoride ion is slightly higher at 120 seconds than at 45 seconds, the standard deviation at this time is quite large and a definite downward trend in fluoride ion concentration is suggested. The highest concentration of HF reported by Machle to be tolerated for one minute by man is 120 ppm. This concentration causes definite smarting of the skin, a sour taste, and irritation of the eyes and respiratory tract. Emergency Exposure Limits (though not specifically relevant to this situation) of hydrogen fluoride are 20 ppm for ten minutes.

It has been reported by Drinker that 10 to 12 breaths of gasoline vapor at concentrations of 2.2 percent by volume cause dizziness in humans. Furthermore, the lower limit of flammability of gasoline mixed with air is reported by Jacobs to be 1.4 percent by volume. Gasoline concentrations of 2.2 percent by volume were reached or exceeded in three of five tests in which samples were successfully collected. Mean concentrations of gasoline are shown graphically in Figure 5.

In several instances the detonation of the HEAT round caused rupture of the fuel tank, spilling large quantities of gasoline into the crew compartment. It should be noted that mean concentrations of gasoline remained approximately the same except when a reflash fire in test No. 6 apparently caused increased vaporization of the fuel.

The National Research Council has recommended that "personnel can be exposed without significant hazard for a maximum of five minutes to normal air at one atmosphere admixed with up to six percent mean concentration by volume of bromotrifluoromethane as a fire extinguishing agent." Concentrations exceeded six percent by volume in nine of the 27 samples. However, five of these nine samples were obtained from test No. 6 in which additional Halon 1301 was used to suppress a reflash fire. Mean concentrations of Halon 1301 are shown graphically in Figure 6. As with fluoride and gasoline, the Halon 1301 concentration reached its highest one second after activation of the system and decreased rapidly.

It has been reported by the du Pont Company that four-minute exposures of three subjects to concentrations of seven to ten percent by volume of Halon 1301 and later studies up to 15 percent by volume caused transient lightheadedness and difficulty in mental concentration with a suggestion of a slight disturbance in equilibrium and reaction time. Electrocardiograms recorded throughout the exposure did not reveal any disturbance in cardiac rhythm.

Evaluation of the data supplied by the Biophysics Division, Biomedical Laboratory, Edgewood Arsenal indicates that of the 20 pigs

Test No	-60	+1	+15	+45	+75	+120	+180	+240	+300
1	X	X	X	X	X	X	X	X	X
2		X	X	M	M		M	M	
3		X	X	X	X	X	X	X	
4	X	X	X	X	X	X			
5	X	F	F	F	F	F			
6	X	X	X	X	X	X			
7	F	F	F	F	F	F			
8		M	M	M	M	M			
9	X	X	X	X	X	X			

M - COLLECTION SYSTEM MALFUNCTION
F - FIRE NOT EXTINGUISHED

FIGURE 3. Sample collection times. Time post ignition in seconds.

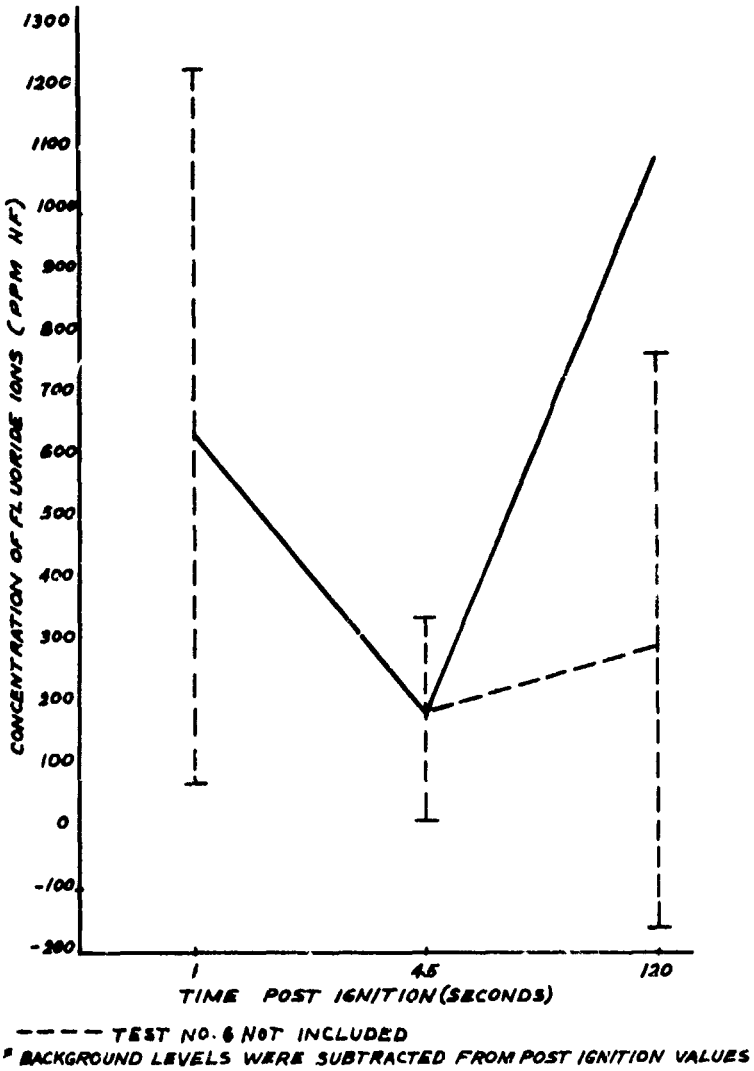


FIGURE 4. Adjusted mean concentration of fluoride ion expressed as hydrogen fluoride (± one standard deviation).

utilized in tests in which the fires were successfully suppressed, three died within fifteen minutes of the detonation of the HEAT round. Necropsy examination of these animals revealed severe bronchial constriction as the probable cause of death. The lungs of the dead pigs remained inflated after the thorax was opened and were not readily deflated even upon manipulation and incision.

Animals which were exposed in vehicles in which the hatches were either left open or blown open by the detonation generally exhibited less pronounced signs of respiratory distress. The animals that were removed from the vehicle beginning at t + 2-1/2 minutes, had less severe respiratory lesions. Animals from the open hatch tests, necropsied ten days following exposure, had either no induced lesions in the respiratory tract or the lesions were mild and in the process of resolving. Some pigs did exhibit mild transient cutaneous erythema which may have been due to either heat or chemical irritation. However, no pigs used

in tests in which the fire was successfully suppressed evidenced distinct cutaneous burns.

Significantly different concentrations of fluoride ion, gasoline and Halon 1301 were detected at different locations within the crew compartment in each of the tests indicating a lack of uniformity in the dispersion of these constituents. Reflash fires occurred, which were manually suppressed. There are a variety of reasons, from hatches left or blown open, to the atmospheric conditions during the test, which may account for these variations.

SUMMARY

Concentrations of fluoride expressed as hydrogen fluoride, inside the crew compartment, usually exceed that considered tolerable by man. Personnel briefly (less than two minutes) exposed to these concentrations will probably experience transient irritation of the eyes, skin and respiratory tract, which may result in coughing and sneezing.

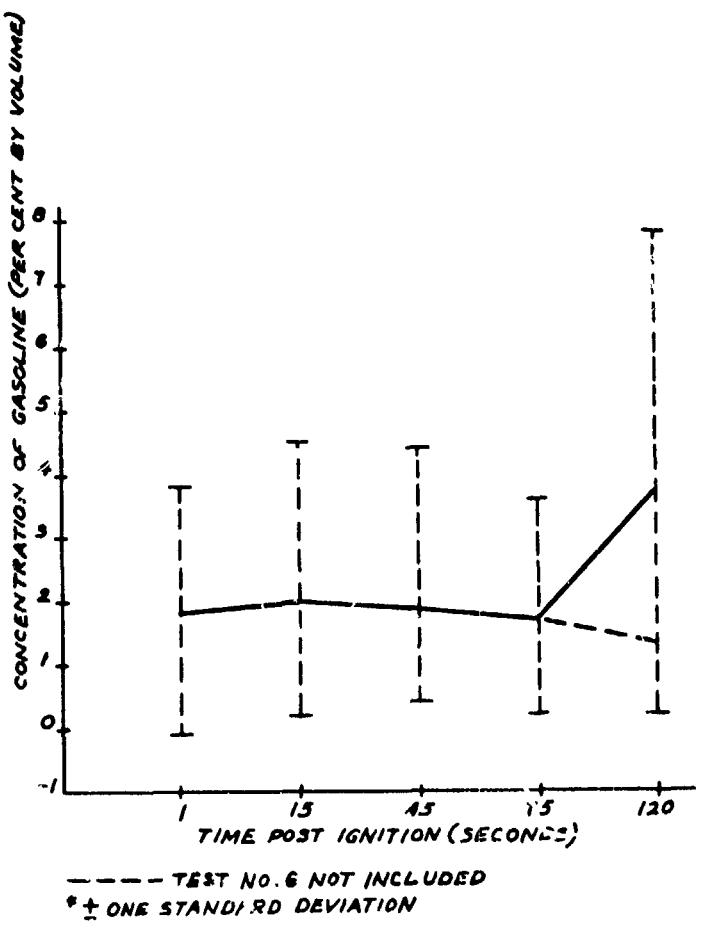


FIGURE 5. Mean concentration of gasoline after ignition and successful suppression of the fire. (± one standard deviation)

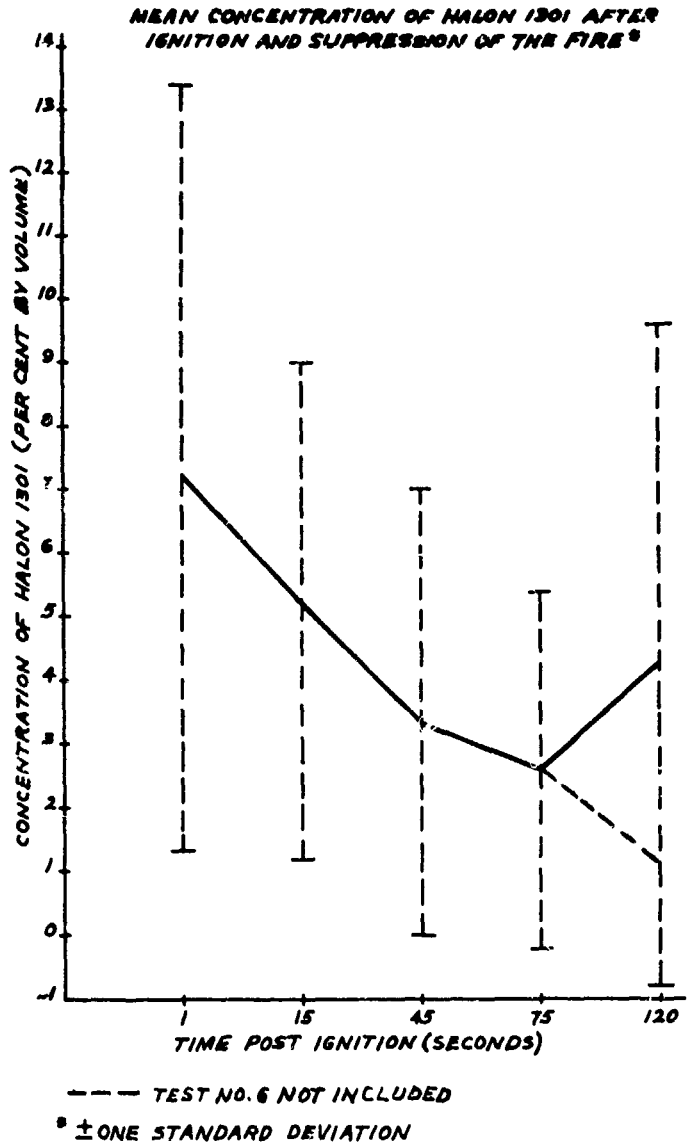


FIGURE 6. Mean concentration of Halon 1301 after ignition and successful suppression of the fire. (± one standard deviation)

The presence of gasoline vapor may cause transient dizziness to personnel in the vehicle. Gasoline concentrations may exceed the lower limit of flammability thereby increasing the possibility of reflash fires.

Concentrations of Halon 1301 found within the M113 crew compartment in these tests were not hazardous to the life of normal healthy people. However, personnel exposed to these concentrations may experience transient dizziness and disorientation. Personnel should be able to evacuate the vehicle in at most two minutes.

It is my opinion that when one weighs the risk of total destruction of the vehicle by fire and subsequent death of the crew members, against the benefits of suppression of the fire, the benefits exceed the risks generated by exposure for less than two minutes to by-products of the fire and/or fire suppression system. Some of the risks generated

by the use of the system can be ameliorated by proper training of the personnel who will utilize the vehicle.

REFERENCES:

1. W. Machle, F. Thamann, K. Kitzmiller and J. Cholak, "The Effects of the Inhalation of Hydrogen Fluoride, 1: the Response Following Exposure to High Concentrations," J. Ind. Hyg. and Tox. 16:129, 1934.

2. P. Drinker, C. P. Yaglou and M. F. Warren, "The Threshold Toxicity of Gasoline Vapor," J. Ind. Hyg. and Tox. 25:225, 1943.

3. M. Jacobs, "Analytical Chemistry of Industrial Poisons, Hazards and Solvents," 1:754, 1949.

4. Technical Bulletin No. S-35A, "Toxicology of du Pont FE 1301 Fire Extinguishing Agent," E. I. du Pont de Nemours & Company, Wilmington, Delaware.

REMARKS

Dr. Walter: Dale E. McDaniel of the United States Coast Guard is our next speaker, and he is going to relate his studies on the "Evaluation of Halon 1301 for Shipboard Use."

EVALUATION OF HALON 1301 FOR SHIPBOARD USE

Dale E. McDaniel

U.S. Coast Guard

DISCLAIMER

The opinions or assertions contained herein are the private ones of the writer and are not to be construed as official or reflecting views of the Commandant or Coast Guard at large.

ABSTRACT

A series of seven full-scale Halon 1301 tests, one agent distribution test and six fire tests, was conducted in the machinery space of the M/V RHODE ISLAND at the Coast Guard's Fire and Safety Testing Facility, Mobile, Alabama. These tests were designed to evaluate the effectiveness of Halon 1301 in extinguishing major machinery space fires and measure the production of toxic gases hydrogen fluoride and hydrogen bromide. The "standard" system was designed to develop a Halon 1301 concentration of 5.65 percent in 7.5 seconds in the machinery space, having a gross volume of approximately 100,000 cubic feet. Fire preburns ranged from one minute to twenty minutes. Temperatures in the compartment ranged from as low as 100°C in some tests to 1140°C in others. Design concentrations were varied between 3.39 and 5.65 percent and discharge times from seven to 28 seconds. Some tests involved sprayed fuels.

All fires were effectively extinguished. There were no reflashes. This indicates that a design concentration of 5.65 percent is adequate to extinguish major machinery space fires. Decomposition products were low in all tests, save the one requiring 28 seconds to discharge. In the 28-second discharge test, some potentially dangerous readings were recorded, suggesting that more rapid discharge times are desirable. It appears that properly designed Halon 1301 systems provide machinery space protection at least equivalent to presently used systems.

INTRODUCTION

Students of the impact of technology on society have observed that events are so interrelated that it is impossible to do just a single thing. Every new technology has not only the intended prime effect but inevitable and sometimes unexpected side effects (1). Such was the case with the advent of mechanical means of ship propulsion. Mechanical propulsion caused a revolution in marine transport, among the most

ancient means of travel known to man. One of the unexpected side effects of this revolution was a marked increase in the frequency and disastrous consequences of shipboard fires. By the mid to late 1800's, public outrage at frequent river steamboat fires and explosions, resulting primarily from propulsion boiler incidents, reached such proportions that the U.S. Congress enacted preventive measures(2). These measures included establishment of the Coast Guard's maritime safety legacy -- the Bureau of Steamboat Inspection -- the first federal government organization concerned with transportation safety. The effect of these steps was to drastically reduce the incidence of boiler explosions and fires. While the number of fires involving propulsion machinery has been reduced, they are still among the most frequent and potentially most disastrous of shipboard casualties. The problem remains of sufficient magnitude that continued research into the prevention and extinguishment of machinery space fires is a significant Coast Guard activity.

The same mixed blessings which accompanied development of mechanical propulsion might be said to have resulted from application of the halon family of fire extinguishing compounds. It has been known for some time that halon compounds are potentially very effective fire extinguishing agents(3). Unlike fire suppressants, such as carbon dioxide, which depend primarily upon reduction of oxygen to a level incapable of supporting combustion, the halon compounds inhibit fire development by chemical reaction. It is possible with these agents to extinguish a fire in an atmosphere containing sufficient oxygen to support combustion. One of the undesirable side effects, however, is the potentially toxic nature of gases produced. Some halon compounds, such as carbon tetrachloride are toxic even in their natural state. Other compounds such as bromotrifluoromethane (Halon 1301), while relatively safe in their natural state, may pyrolyze when exposed to flames or high temperature creating toxic products. Thus, considerable concern has been expressed regarding large-scale use of the halon agents due to possible adverse affects on personnel in the vicinity.

One of the most weight-effective of the halon agents is Halon 1301; it is also one of the least toxic in the natural state. A great deal of basic and practical research has been conducted on its effectiveness as a fire-fighting agent. It has been employed for a number of applications having unique requirements, such as weight-critical marine vehicles, primarily hydrofoils and hovercraft. Usage aboard commercial marine vehicles in the United States was restricted, however, to small unmanned compartments aboard specific types of vessels. The reasons for such restrictions were twofold:

1. the concern over potentially dangerous concentration of toxic gases, and

2. the lack of demonstrated effectiveness of Halon 1301 in large-scale, severe fire situations.

In view of the foregoing circumstances, it was believed appropriate to conduct an evaluation of Halon 1301 systems on large-scale

machinery space fires. Three organizations -- The Ansul Company, E. I. du Pont de Nemours & Company and the Cardox Division of Chemtron Corporation -- proposed that such tests be undertaken at the Coast Guard's Shipboard Fire and Safety Testing Facility at Mobile, Alabama. This proposal was endorsed by the Coast Guard and its ad hoc test advisory group which offers guidance on test planning.

TEST FACILITY

A complete description of the test facility and its operation has been provided elsewhere (4). However, for those not familiar with the facility, a brief description will assist in visualizing the testing program. The Coast Guard Sponsored Shipboard Fire and Safety Testing Facility was established in 1969, culminating the efforts of an industry triad begun many years previous. It consists of an old T-1 tanker diked into a slip dredged in Little Sand Island, located in Mobile Bay, across the ship channel from the city of Mobile itself. Original equipment aboard the vessel is inoperative; all support services such as electrical power and fire-fighting are provided externally. Access to the island is by water.

The test ship itself, the M/V RHODE ISLAND, is an 8500-gross-ton tanker constructed in 1937. She was an oddity among U.S. flag ships in that propulsion was by a diesel. Three auxiliary boilers are fitted, primarily for operation of steam-power machinery. The main propulsion diesel is situated in an aft machinery space having a gross volume of approximately 100,000 cubic feet. Contiguous with this space, and separable from it, is a much smaller space housing the auxiliary boilers. A schematic profile of the space is shown in Figure 1. For the Halon 1301 tests, the boiler space was closed off from the machinery space. The tank top of the machinery space has a total area of roughly 2200 square feet and a net area (excluding the main engine foundation) of about 1600 square feet. The total height of the space is approximately 50 feet.

Prior to the Halon 1301 tests, the machinery space had been employed for two series of tests intended to evaluate the effectiveness of various types of fire detection devices (5). These tests employed small pan fires. Additionally, the space had been employed for full-scale tests of a low-pressure carbon dioxide extinguishing system, which was also employed as the primary backup for most of the Halon 1301 tests. Prior tests provided essential experience in conduct of large-scale tests aboard the vessel and, additionally, provided a comparative base against which to measure performance of the Halon 1301 systems.

EVOLUTION OF MACHINERY SPACE FIRE EXTINGUISHING SYSTEMS

The fire hazard present in machinery spaces was mentioned in the introduction. Fire extinguishing technology probably first began to really gain on this machinery space hazard with introduction of carbon dioxide extinguishing systems. Initially, protection of boiler rooms was by means of bilge-flooding type carbon dioxide system designed using a volume factor of 36 $ft.^3/lb$. Tests conducted at Ft. McHenry aboard the GASPAR DE PORTOLA in 1944 showed that these systems were

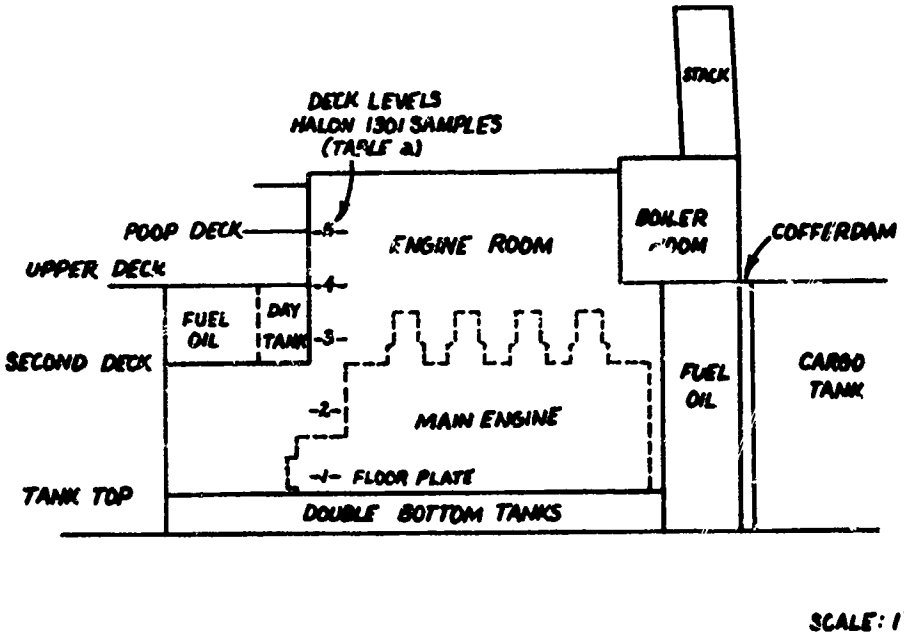


FIGURE 1. M/V RHODE ISLAND profile of machinery space.

effective, providing they were released within the first few minutes of a fire (8). Once a machinery space fire became fully established although the bilge flooding systems provided temporary suppression, reflash occurred. This prompted work in two directions, one by Lloyd Layman who became intrigued with the concept of controlling the flow of air to a machinery space fire and suppressing it with very small amounts of water spray. This technique was employed successfully several times in 1944 on the GASPAR DE PORTOLA. The technique does, however, require a thoroughly heated space and careful application of water. Some attempts aboard the GASPAR DE PORTOLA met with failure as did one recent attempt aboard the RHODE ISLAND. It is probably an impractical technique because it requires skills beyond those of most shipboard crews.

The second direction of work was aimed at improvement of installed carbon dioxide systems. This resulted in new design requirements being promulgated in 1952 calling for a flooding factor of 22 cubic feet per pound, a significant improvement over previous requirements. Theoretically, such a system is capable of a 33.5 percent concentration of carbon dioxide and is sufficient to reduce the oxygen content of the atmosphere to 13.9 percent under non-fire conditions. The new arrangement had not been tested full scale until the fires preceding the Halon 1301 tests in 1970. The new requirements proved successful. From these latest CO_2 tests, using a low-pressure system, it appears that there is an adequate margin of safety in present CO_2 design requirements, providing the main air intakes are closed prior to release of the agent. Tests with main air intakes open using the present CO_2 requirements have not yet been conducted.

Carbon dioxide systems, usually of the high-pressure type, have a generally satisfactory record of effectiveness in actual shipboard

fires. While complete statistics are not available, the author is aware of only a very limited number of incidents where, due to various unique circumstances, the installed system was not effective. It is obvious, of course, that when a total flooding carbon dioxide system is released, the space becomes incapable of supporting human life. The virtue of extinguishment carries a possible adverse side effect of asphyxiation. This has reportedly made some ship captains reluctant to release the installed carbon dioxide system until the last possible moment. Should Halon 1301 prove effective, its low toxicity at ambient temperature would be an apparent asset. Nonetheless, the favorable records of total flooding carbon dioxide systems, coupled with the recent full-scale tests aboard the RHODE ISLAND, provide a valuable reference point.

The present trend in fire extinguishing systems seems to be toward a totally engineered system. That is, systems are designed to automatically detect and extinguish a fire. Such systems are advantageous from several standpoints. For example, ideally they provide continuous protection, minimize damage and reduce the likelihood of pyrolysis of extinguishing agent when this danger exists. This technique has not been introduced in any significant way aboard merchant ships for several reasons:

1. automatic fire detection in machinery spaces has not yet reached a stage of development that systems can be considered fully effective and reliable;

2. automatic release of the system, in event of a false alarm, deprives the vessel of its primary fire extinguishing capability; and

3. release of the system requires shut down of ventilation and other services which may be untimely and jeopardize, say, in the case of delicate maneuvering, critical navigational capability.

Eventually, these limitations may be eliminated and automatic systems installed. For the present, however, the Coast Guard and the ad hoc advisory committee believed that manual actuation of the system should be presumed as the basis of full-scale testing. This dictates that systems must be capable of extinguishing fires of maximum expected intensity. Should such a system be coupled with automatic detection and release, even failure of the automatic control would not render the system ineffective if it is proven effective in very severe tests.

HALON 1301 TEST PLANNING

It was believed by many that Halon 1301 could be designed to have an effectiveness for machinery space fires at least equivalent to a total flooding carbon dioxide system. In addition to the lower risk to life at ambient temperatures, Halon 1301 reportedly has other advantages such as requiring considerably less agent and consequently less storage space, as well as being capable of storage at considerable lower pressures at ambient temperature.

A large-scale program, consisting of five separate tests, was devised by E. I. du Pont de Nemours & Company and the Ansul Company and designed to measure:

1. the ability of Halon 1301 to extinguish large-scale machinery space fires;

2. the margin of safety inherent in Halon 1301 designs, as compared to carbon dioxide, and

3. the toxic products of pyrolysis both within the space and in contiguous compartments.

The Halon 1301 system to be used was the "standard" type using nitrogen to superpressurize the container to approximately 600 psig. The "standard" system believed suitable for protection of the machinery space hazard was one developing a concentration of 5.65 percent Halon 1301 in 7.5 seconds. This was generally the base from which test parameters were varied.

At the same time du Pont and the Cardox Division of Chemtron Corporation proposed two additional tests which would supplement the previous objectives and also provide information on:

1. the practicality of heating Halon 1301 to obtain discharge pressure and

2. suitability of using installed carbon dioxide equipment, including piping, for delivering Halon 1301.

The entire testing program was to be coordinated by the U.S. Coast Guard. A summary of the testing program is shown in Table 1.

TEST ARRANGEMENT

The nitrogen superpressurized system was designed to deliver the gas through a total of five nozzles located at three different levels on the forward boundary of the compartment and directed horizontally into the space. Selection of the number and disposition of nozzles was based upon previous Halon 1301 distribution tests. In general, the system was designed in accordance with the standards set forth in NFPA No. 12A -- Halogenated Extinguishing Agent Systems, Halon 1301. A schematic of the arrangement is shown in Figure 2.

For the heated system, Halon 1301 was delivered through the installed CO_2 piping. Carbon dioxide discharge nozzles were replaced by more suitable ones and were located primarily at a single level and directed downward. A schematic of this arrangement is shown in Figure 3.

Fuel consisted of marine diesel (flash point 130°-150°F) which was floated on water in such a manner as to cover the entire surface of the bilge. Due to the slight list and trim of the vessel, the fuel surface was approximately one-half above and one-half below the floor

TABLE 1

Test Plan

Test No.	System Type	Preburn Time	Calculated Halon 1301 Concentration[a]	Lbs of Agent	Design Discharge Time
0	Nitrogen Superpressurized	0 min.	5.65%	2340	7.5 sec.
1	"	10 min.	5.65%	2340	7.5 sec.
2	"	10 min.	4.40%	1800	4.7 sec.
3	"	1 min.	4.40%	1800	4.7 sec.
4	"	20 min.	5.65%	2340	7.5 sec.
5	Heated	1 min.	3.39%	1301	18. sec.
6	"	10 min.	4.64%	1903	28. sec.

a) Concentration based on the gross volume of the space, without reduction for volume occupied by main engine, etc., at 70°F.

plates. Floor plates are steel and form a semi-tight enclosure approximately four feet above the tank top level. Some floor plates were removed in areas where fuel did not extend above the floor plate surface to open that area directly to the atmosphere of the machinery space. During two of the tests, pressurized spray fuel was injected into the space.

The diesel fuel was primed with five to ten gallons naptha and/or methyl ethyl ketone in way of four flare ignitors arranged to ensure rapid involvement of the entire compartment. The ignitors were activated remotely by shorting out high resistance coiled electrical wire.

Ventilation during the fire was provided by six rectangular ventilation ducts, each of roughly nine square feet cross sectional area. The ducts are arranged in symmetrical pairs, one port and one starboard, one pair located forward, one midlength of the space and the other aft. The fore and after pairs of ducts extended from outside of the space to within about 12 feet of the floorplates, the midship's pair terminated at the upper deck level, about 25 feet above the floor plates. Power supply ventilation fans, each capable of delivering 37,500 cfm were located at the upper end of the forward starboard and port aft ducts. These fans were operated during the entire preburn periods.

MEASUREMENTS

Arrangements were made to continuously monitor temperatures by means of twenty-four thermocouples spaced throughout the compartment. Continuous readings were also made of oxygen and carbon monoxide. Single samples were drawn for later analysis of the concentration of Halon 1301, hydrogen fluoride and hydrogen bromide. Sampling points are shown in Figures 4 and 5.

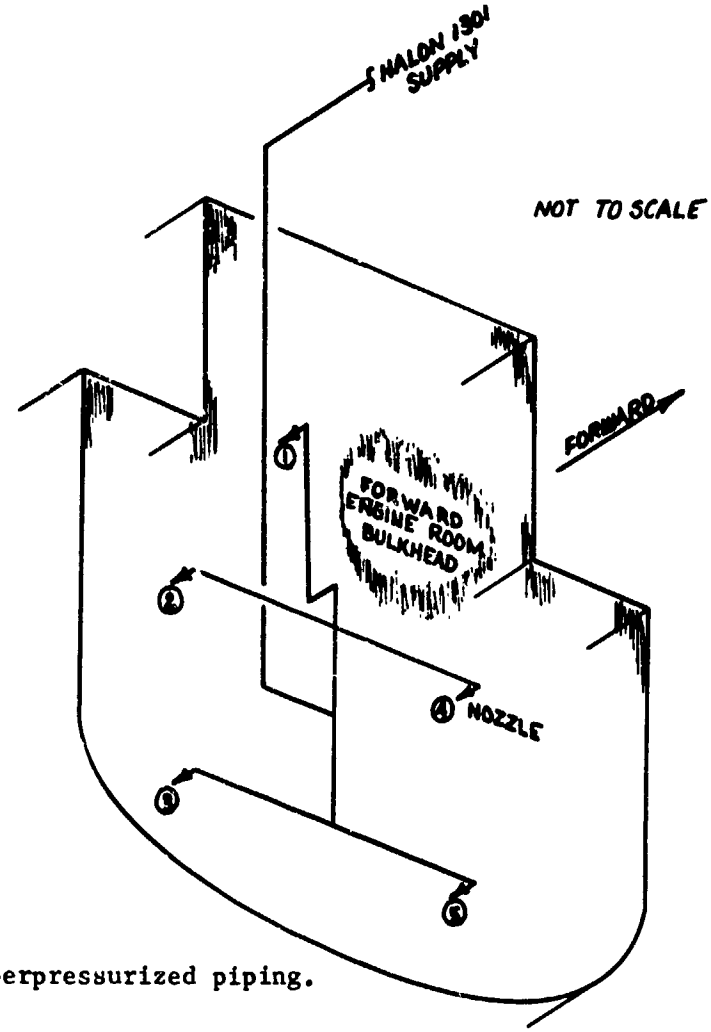


FIGURE 2. Superpressurized piping.

Discharge times for the nitrogen pressurized tests were measured in two ways. During the non-fire distribution test a photographic record of tank pressure was made and compared to audio indications of discharge. Discharge times during later tests were by audio monitoring and stop watch. The quantity of agent used was determined by weighing the tank and contents before and after test. Discharge times during the superheated tests were controlled by means of a manually operated stop valve and confirmed by recorded times to develop final Halon 1301 concentrations.

Temperature, carbon monoxide and oxygen readings were transmitted to the nearby National Bureau of Standards instrumentation van where they were entered in a continuous recording data-logger. Analysis of gas samples was made by du Pont. Analysis for hydrogen fluoride and hydrogen bromide was made using specific ion electrodes. For Halon 1301 samples, analysis was made by gas chromotography. Greater details of the analytical procedure are contained in references 6 and 7.

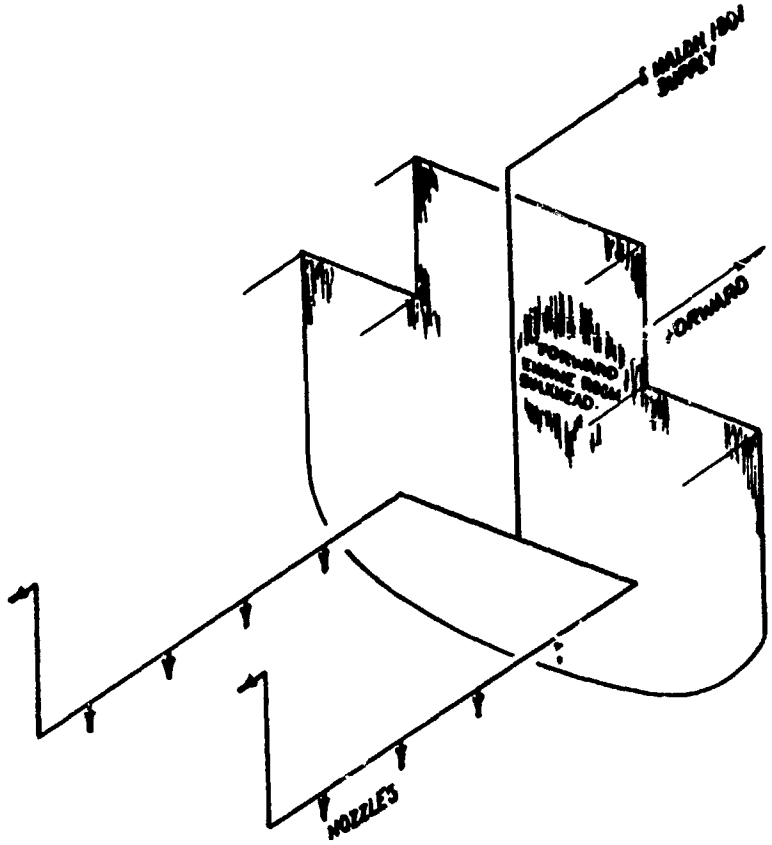


FIGURE 3. Heated system piping. NOT TO SCALE

CONDUCT OF THE TESTS

A complete description of the conduct of individual tests is given in the official Coast Guard report, expected to be published by the time this paper is presented and need not be repeated here (9). In general, the procedure was the same for each individual test with the only variable being the preburn time. An exception was Test 0 which was intended only to measure agent distribution and did not involve a fire. Flare ignitors were put in place and primer added to the fuel in way of each ignitor. All personnel were then evacuated from the space and flares activated electrically. Activation of the flare ignitors started an electrical clock located in the test van. Stop watches were also started at the same time. Once it became apparent that the diesel fuel was involved in the fire, the power blowers were activated. This started the preburn period. One minute prior to discharge of the agent at the end of the preburn period, the fans were shut down and ventilators covered with the exception of test No. 4 when one ventilator remained uncovered for some period after agent discharge. If fuel was to be sprayed into the space during the test, fuel sprayers were started at the same time. The Halon 1301 system was released at the end of the

specified preburn time. Samples were taken for analysis of Halon 1301/ air/CO_2 forty seconds after release of the systems. Samples for analysis of hydrogen fluoride and hydrogen bromide samples were taken fifty seconds after agent discharge. Fuel spray, if used, was stopped one minute after discharge when it was determined that the primary risk of reflash had passed.

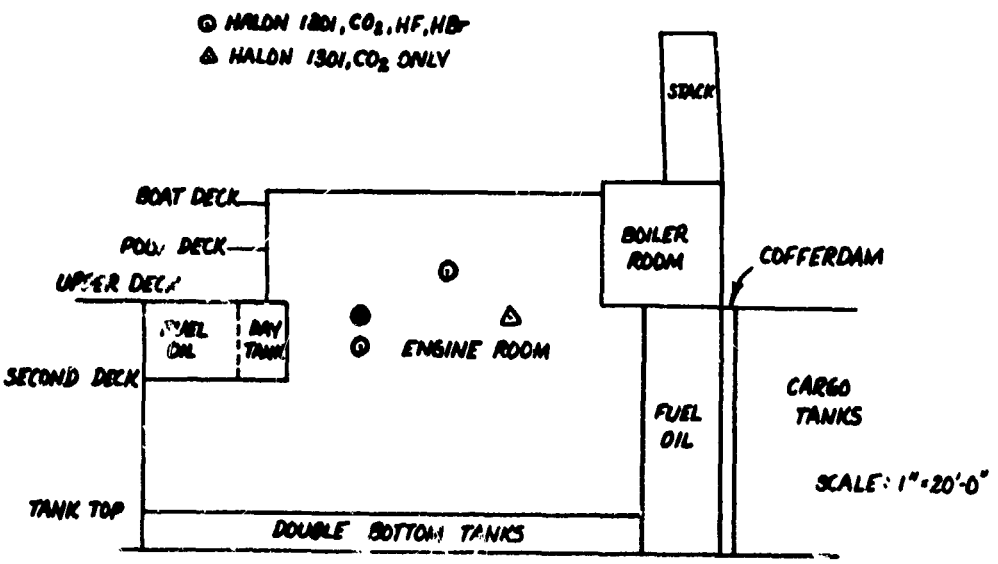
TESTS RESULTS

Distribution Test

The first test, Test 0, was concerned only with agent distribution; there was no fire. During discharge of the agent the bottom half of a dutch door (2' x 3') in the upper portion of the machinery casing was blown open. All other permanent openings to the space were closed reasonably tight.

Following discharge the space was entered and readings of Halon 1301 distribution made using two Gow-Mac meters. Readings were made beginning at the lowest deck level and ending at the highest.

FIGURE 4
MACHINERY SPACE
PROFILE OF GAS SAMPLE POINTS



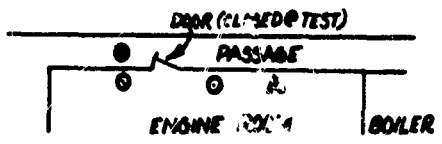


FIGURE 5
DECK PLAN
SAMPLE POINTS

FIGURES 4&5 - GAS SAMPLE POINTS

FIGURES 4, 5. Gas sample points.

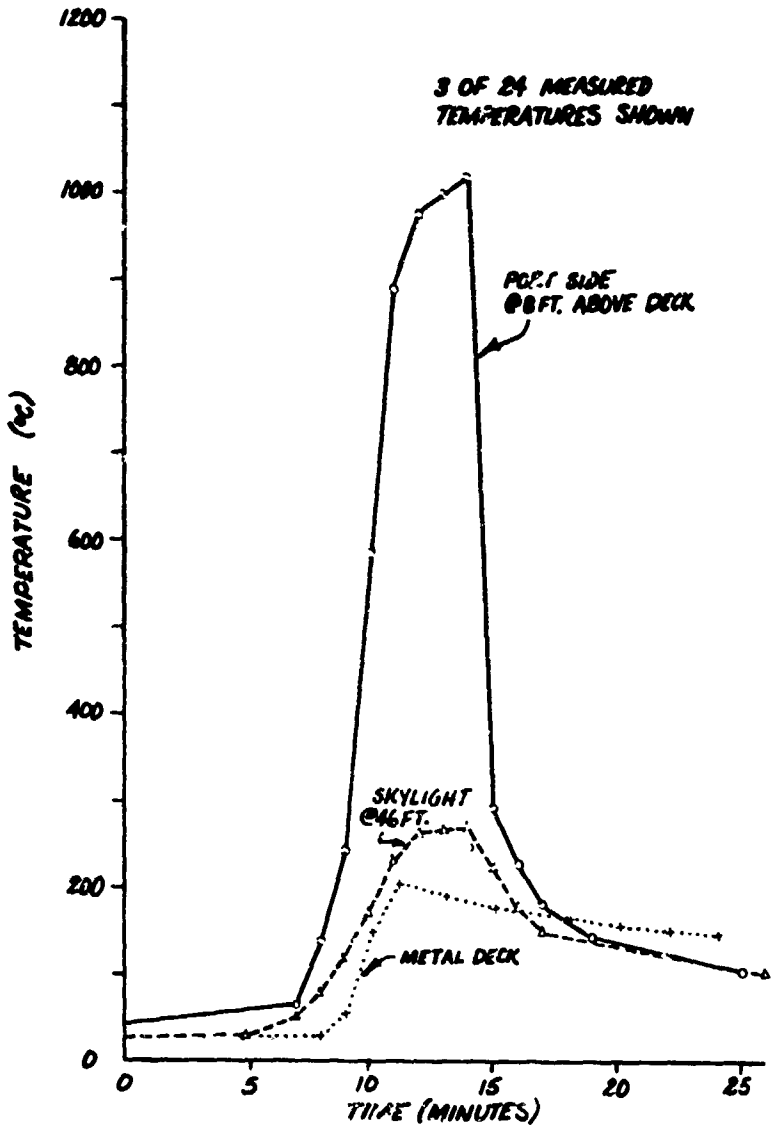


FIGURE 6. Typical temperatures -- 10 minute Halon 1301 test.

Additionally, evacuated bottle samples were taken at the same fixed locations and using the same sampling techniques as during later tests -- these at twenty-five seconds following discharge. No adverse effects were suffered by personnel entering the space, except for the usual lowered pitch of the voice (viewed by some as a favorable and not an adverse circumstance). Halon 1301 distribution is shown in Table (a). The intended 7.5 second discharge was not achieved; discharge required 10.9 seconds. As a result, nozzles were replaced with other nozzles having larger orifices.

Fire Tests

The remaining tests were conducted to evaluate system effectiveness on fires of varying intensity. Extinguishing concentrations were

TABLE (2)

Distribution of Halon 1301

Test 0 -- No Fire -- Design Concentration 5.6 %

Concentration (Volume Percent)

Deck Level[a]	Gow-Mac-1	Gow-Mac-2	Evacuated Bottle
1	10.9[b] (0 ft)[d]	---	---
2	6.4 (10 ft)	6.3	---
3	4.8 (17 ft)	6.0	0.4[c] (20 ft)[d]
4	4.0 (25 ft)	3.[illegible]	6.1 (20 ft)
5	2.0 (35 ft)	---	3.5 (35 ft)

a) See Figure 1.
b) Concentration is suspiciously high. Perhaps due to premature instrument reading, before equilibrium distribution reached.
c) Very low reading probably attributable to leaky solenoid valve.
d) Height above floor plates.

also varied to evaluate the margin of effectiveness inherent in required design requirements. Finally, the discharge time was varied to determine the effect of this parameter on extinguishing effectiveness and toxic product development. As previously mentioned, the "standard" system was to develop a 5.65 percent concentration in 7.5 seconds.

All fires were effectively extinguished immediately. Extinguishment was generally accompanied by a sharp reduction in temperatures recorded within the compartment. Following extinguishment and collection of the gas samples, the space was allowed to "soak." In no case did reflash occur. Once the space had cooled to a point that there was no further danger of reflash, the space was ventilated and entered to inspect for damage and prepare for the next test.

Results of the tests are summarized by Tables 2 and 3.

Table 2 demonstrates that for the particular arrangements tested, gross volume concentrations as low as 4.4 percent are capable of extinguishing a major machinery space bilge fire involving diesel oil fuel. Design concentrations of 3.39 percent are adequate to extinguish incipient bilge fires.

The fires tended to be self-limiting in terms of burning rates due to the severe limitations on available oxygen. This is seen particularly from the graph shown in Figure 7. Unfortunately, due to a malfunction of recording equipment, it was not possible to record oxygen readings during tests Nos. 3 to 6. However, readings derived during

TABLE 2

Test No.	Design Conc.	Design Discharge Time	Actual Discharge Time	Preburn Time	Spray Fuel
1	5.65%	7.5 sec.	10 sec.	10 min.	yes
2	4.40	4.7	7	10	yes
3	4.40	4.7	7	1	no
4	5.65	7.5	10	20	no
5	3.39	a	18	1	no
6	4.64	a	28	10	no

a) not calculated prior to discharge.

tests Nos. 1 and 2 are sufficiently consistent that there is no reason to believe subsequent tests were not similar. For comparison purposes, oxygen levels recorded during the carbon dioxide tests are shown. It will be noticed that the levels during CO_2 and Halon 1301 tests are not strikingly different. Several observations should be made in this regard:

1. as mentioned previously, even though the fires were oxygen-limited and readings would indicate inadequate oxygen to sustain a fire, the burning was intense. It was not possible to extinguish the fires by "sealing" the space and/or applying water spray;

2. intensity of the fires, as measured by temperatures within the compartment were considerably more severe than machinery space fires conducted aboard the GASPAR DE PORTOLA in 1945;

3. successful extinguishment during each of the tests is in some ways disturbing. When all the fires go out, we really don't know what is being done correctly, or how much margin of error exists in which parameters. It is expected that some of these questions will be gradually answered as additional testing experience is gained.

Unfortunately, as will be noted from Table 3, test fire No. 4 was so intense that the equipment for analyzing hydrogen fluoride and hydrogen bromide was destroyed. This necessitated improvising single-point sampling mechanisms for the later tests. From the reports of those present during test No. 4, however, the odor of smoke emanating from the space during the extinguishing process did not differ noticeably from that of previous tests.

It has been reported by Dr. Irving N. Sax that the approximate lethal concentrations for 15-minute exposure and the dangerous concentrations for short exposures are as follows (10):

Compound	ALC (15 min.) (ppm by Volume in Air)	Dangerous Concentration (ppm by vol.)
Hydrogen Fluoride	2500	50-250
Hydrogen Bromide	4750	----

Readings were not made of concentrations of other potentially dangerous decomposition products such as bromide, carbonyl fluoride and carbonyl bromide.

It will be noted that, assuming the olfactory analysis during test No. 4 indicates the absence of dangerous concentrations of decomposition products, that only during test No. 6 did potentially hazardour concentrations of pyrolysis products develop. This is believed to be attributable primarily to the longer discharge time (28 seconds) required for release of Halon 1301. Fires of similar intensity (Nos. 1 and 2) in which the agent was discharged more quickly (ten and seven

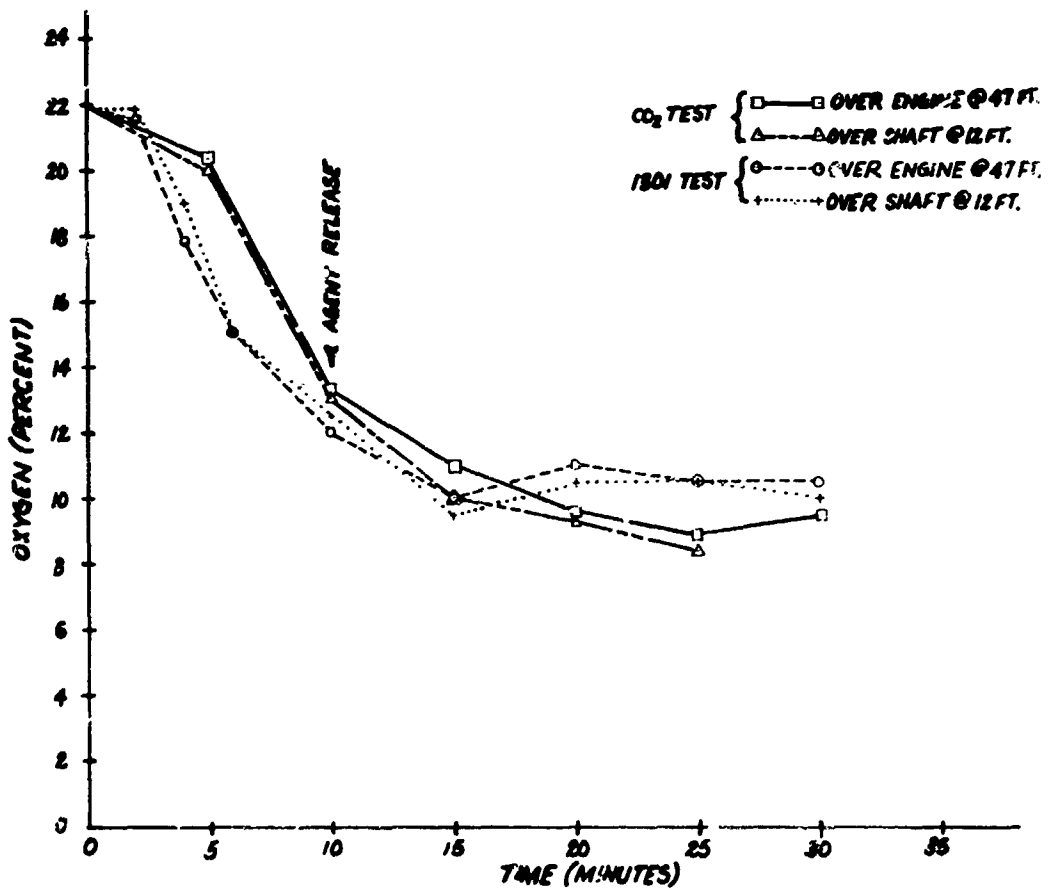


FIGURE 7. Oxygen level -- CO_2 and Halon 1301 extinguishing tests.

TABLE 3

Gas Analysis and Maximum Temperatures

Height of Reading[a]

Discharge Time	Test \ Reading	46'					35'							25'					20'							8'					Companionway[b] (25')				
		T	HF	HBr	1301	CO_2	HF	HBr	T	HF	HBr	1301	CO_2	T	HF	HBr	1301	CO_2
10 sec.	1	210°C	3.5	0.9	6.7	3.4	2.7	0.5	200°C	2.2	0.6	8.0	3.5	530°C	1.0	0.4	3.0	5.0
7 sec.	2	240	2.7	1.1	6.4	4.4	4.2	0.9	190	2.7	1.6	6.4	4.0	700	0.6	0.4	0.1	7.5
7 sec.	3	30	9.6	2.6	3.1	0.4	5.1	0.9	40	12.0	0.9	3.5	0.3	110	0.6	0.3	2.3	0.4
10 sec.	4	460	(c)	(c)	0.1[e]	3.1	(c)	(c)	1100	(c)	(c)	6.4	4.9	1140	(c)	(c)	12.7	7.4
18 sec.	5	30	(c)	(c)	(d)	(c)	(c)	(c)	40	0.1	0.6	(d)	(c)	60	(c)	(c)	(d)	(c)
28 sec.	6	260	(c)	(c)	4.4	5.3	(c)	(c)	180	230	68	7.8	3.7	1020	(c)	(c)	0.1	0.4

LEGEND:
- T = Maximum temperature @ level (°C)
- HF = Hydrogen Fluoride (parts per million)
- HBr = Hydrogen Bromide (parts per million)
- 1301 = Halon 1301 (volume %)
- CO_2 = Carbon Dioxide (volume %)

(a) - height above floor plates
(b) - outside of machinery space
(c) - equipment destroyed by intense fire No. 4, jury rig system for tests Nos. 5 and 6
(d) - insufficient evacuated bottles for both tests Nos. 5 and 6
(e) - value highly suspect, probably due to equipment failure

seconds, respectively) resulted in very low concentrations of hydrogen fluoride and hydrogen bromide.

In general, the concentrations of hydrogen fluoride and hydrogen bromide recorded were much lower than those expected prior to the start of testing. This might be attributable to one of several factors: intensity of fire in the space, obscuration of flame, or agent discharge time. While low concentrations during fires Nos. 3 and 5 might be accounted for by low-fire intensities, this cannot explain fires Nos. 1 and 2, which reached air temperatures of 530°C and 700°C and metal temperatures of 400°C and 300°C respectively. Test No. 5 was more intense in localized areas than tests Nos. 1 and 2 but, being one of degree, this seems unlikely to be a primary reason for higher concentrations during test No. 6. Similarly, flame obscuration was nearly identical in all tests and should not account for any major difference in toxic concentrations. This leaves only time of discharge as a primary cause. During intense fires, the entire piping system becomes heated (recall there is considerably more mass in the piping system for tests Nos. 5 and 6 than for other tests--Figures 2 and 3) prolonging the period of vapor discharge. This prolonged discharge of vapor coupled with longer times to develop extinguishing concentrations would result in greater pyrolysis. The longer discharge seems a plausible primary cause of increased toxic product concentration.

As a practical matter, the production of toxic products did not seem to be a problem during any of the tests. At the time samples were taken within the space, even the high readings during test No. 6, the atmosphere was totally unsuited for human occupation without special protective equipment -- disregarding the pyrolysis products. Oxygen was depleted, temperatures excessive, smoke unbearable and CO concentration very high. For example, carbon monoxide readings during the first three tests showed:

Test No.	CO off scale at:[a]
1	6-1/2 minutes
2	4
3	(reads 0.08% @ 4 minutes)

(a) full scale is 0.2% CO

Equipment failed during test No. 4 precluding subsequent CO readings. Additionally, at no time did personnel outside of the space on the open deck notice conditions more objectionable than with smoke from a fire alone. This observation must modify somewhat the unsubstantiated belief that no dangerous concentrations were present in the space during test No. 4.

In the companionway adjacent to the space, it will be observed that, with the exception of CO_2 readings and one Halon 1301 reading, concentrations were always below those within the space itself. Thus, even though fire gases obviously entered the companionway, as evidenced by CO_2 and Halon 1301 readings, from the standpoint of toxic products, this area was relatively protected.

As a result, for all of the systems tested, it would seem that the major risk to personnel from pyrolysis products might result from premature entry into the space following successful extinguishment and/or some equipment malfunction which might result in only partial system discharge and partial extinguishment.

Even though the findings do not fully substantiate absence of dangerous concentrations during the 20-minute preburn, and even though there were no ill effects during the 28-second discharge, prudence dictates that Halon 1301 systems should be designed with a discharge time no greater than ten seconds. This proved a safe discharge time for all tests for which quantifiable results are available. Similarly, the 28-second discharge did produce gas concentrations which under other circumstances might be dangerous. Finally, a ten-second discharge requirement should not prove burdensome for new systems.

Referring again to Table 3, it will be observed that, with the exception of test No. 3, recorded concentrations of Halon 1301 were greater than the design concentrations. The apparent anomaly of test No. 3 can perhaps be accounted for by the lower fire intensity which resulted in less complete mixing of the atmosphere. Under this theory, at the lower levels the design concentration of 4.4 percent would be markedly exceeded.

Tests 0 (no-fire), 1 and 4, all with design concentrations of 5.65 percent, show remarkably similar concentrations (Tables a and 3). The comparability of results would indicate that with reasonably tight spaces, not a great deal of agent is lost due to fire convection. Results also show some difference in Halon 1301 concentrations at the 20-foot and 35-foot levels, although this difference is accentuated under conditions of no fire (Table a), apparently due to less turbulence in the space. The system used during test No. 6 discharged the agent downward which resulted in a greater gradation of concentration between the two elevations.

In respect of the discharge times of the superpressurized system (tests Nos. 1 to 4), it will be observed from Table 2 that the actual discharge times exceeded the design discharge times by 25-50 percent, greater for the shorter design times. This occurred even after replacement of the nozzle orifices following test No. 0 which was intended to reduce the required time of discharge. This is perhaps explained partially by the heated piping system. Nonetheless, future system designs should take account of these factors so that intended discharge times can be achieved by actual systems.

SUMMARY

This series of full-scale tests demonstrates that short-discharge (28 seconds or less) Halon 1301 extinguishing systems, with a gross volume design concentration of 5.65 percent, will effectively extinguish incipient and fully developed fires involving diesel oil fuel in the bilges of machinery spaces. Such systems are also capable of extinguishing fires involving sprayed fuel. These systems are at least

equivalent in fire extinguishing effectiveness to presently installed fixed carbon dioxide extinguishing systems.

The tests also indicate that when the discharge time of the system is ten seconds or less, concentrations of toxic gases do not increase the risk of personnel injury. No dangerous concentrations of hydrogen fluoride or hydrogen bromide develop either inside or outside of the space (The space itself is, of course, untenable due to numerous other conditions associated with the fire.) When the discharge time was increased to 28 seconds, some potentially dangerous concentrations were recorded within the space less than one minute following discharge. Under conditions which differ from the test situation, such concentrations might be unacceptable suggesting, for the present at least, that the system should discharge in ten seconds or less. The superpressurized system (tests 0 to 4) was designed to discharge a full charge of agent in 7.5 seconds but actual discharge times were never less than ten seconds.

There are indications that a superheated system can be designed successfully, providing discharge times are reduced to approximate those of superpressurized systems.

A properly designed Halon 1301 system, therefore, appears to afford adequate, safe protection against machinery space fires.

FOOTNOTES AND REFERENCES:

1. As an example, see D. A. Schon, Technology and Change.

2. A complete description of development of river steamboat transportation, including its hazardous nature, is contained in Louis C. Hunter, Steamboats on the Western Rivers, Harvard University Press, Cambridge, 1949.

3. A classic study in this field was conducted in 1950. See Final Report on Fire Extinguishing Agents (AD 654 322), Purdue Research Foundation and Department of Chemistry, Purdue University, under contract to U.S. Army Engineers Research and Development Laboratories, Ft. Belvoir, Va., June 30, 1950.

4. D. E. McDaniel, "Marine Environmental Fire and Safety Test Facility," Proceedings (CG-129), 27:183-187, October 1970, published by U.S. Coast Guard. Also published in Proceedings of Twelfth Annual Marine Chemists' Association Seminar, July 7-10, 1970.

5. Reports of these tests are available from the Coast Guard. Refer to Report of Machinery Space Fire Detecting Tests, Phase 1 (Kerlin and McDaniel) and Phase II (Kerlin).

6. J. A. Floria, "U.S. Coast Guard Shipboard Fire Extinguishing Tests in Conjunction with The Ansul Company," Technical Report No. KSS-7105, Freon Products Laboratory, E. I. du Pont de Nemours & Company, January 20, 1971.

7. J. A. Floria, "U.S. Coast Guard Shipboard Fire Extinguishing Tests by Cardox Using Freon 1301 in Carbon Dioxide Equipment," Technical Report No. KSS-7105A, Freon Products Laboratory, E. I. du Pont de Nemours & Company, January 20, 1971.

8. L. Layman, R. C. Stange and C. M. Jones, "Report on a Study of the Control and Extinguishment of Fuel Oil Fires in the Machinery Spaces of Vessels," U.S. Coast Guard, June 1, 1945.

9. D. F. Sheehan, "An Investigation into the Effectiveness of Halon 1301 (Bromotrifluoromethane $CBrF_3$) as an Extinguishing Agent for Shipboard Machinery Space Fires," to be available through the Coast Guard or the clearinghouse for Federal Technical and Scientific Information, Springfield, Va.

10. I. N. Sax, Dangerous Properties of Industrial Materials, Second Edition, Section 12, Reinhold Publishing Corporation, New York, N.Y., 1963.

REMARKS

Dr. Walter: B. P. Botteri, of the Aero Propulsion Laboratory, United States Air Force, is going to present a paper on "Aircraft Applications of Halogenated Hydrocarbon Fire Extinguishing Agents."

AIRCRAFT APPLICATIONS OF HALOGENATED HYDROCARBON FIRE EXTINGUISHING AGENTS

B. P. Botteri, R. E. Cretcher and W. R. Kane

Wright-Patterson Air Force Base

INTRODUCTION

Aircraft inherently possess a diversity of potential fire and explosion hazards. Although the principal threat is associated with the hydrocarbon fuel, attention must also be given to other sources of fire such as hydraulic fluids, lubricating oils, interior cabin materials, electrical equipment, and various cargo. In addition to the variety of potential combustibles a number of fire initiation sources are also possible such as hot surfaces, friction sparks, electrical arcs and sparks, hot gases and, particularly for military aircraft, gunfire. The achievement of an effective fire protection capability for aircraft entails the critical assessment of the probability of a combustible and an ignition source coming together; the application of preventative measures in the design of the aircraft to minimize such an occurrence; and incorporation of appropriate fire surveillance and suppression techniques to counteract the remaining "high risk" fire problems. This technical discussion will focus on the fire and explosion suppression problem, the last line of defense against the destructive propagation of fire. A number of suppression methods are available and for an aircraft, depending on the level of fire protection required, several suppression methods may be employed. In accordance with the purpose of this conference we will principally address the use of halogenated hydrocarbon fire extinguishants for the U.S. Air Force aircraft fire protection problem.

Although it is apparent that a variety of fire and explosion possibilities exist on-board an aircraft, for the purposes of this discussion it is necessary to narrow the fire problem possibilities to those of principal concern. These are: engine and auxiliary power installations, fuel tanks, and habitable and cargo compartments. In analyzing the applications of halogenated hydrocarbon fire extinguishants to these aircraft fire problem areas, our approach will be to qualitatively describe the nature of the fire problem in each area, review the state-of-the-art fire suppression techniques which could be applicable, identify the preferred technique and the basis for its selection, and, in those cases where use of halogenated hydrocarbon extinguishants is preferred, to review their overall practical performance record.

PROPERTIES OF HALOGENATED HYDROCARBON FIRE EXTINGUISHANTS

A large number of halogenated hydrocarbon compounds possessing fire extinguishing properties have been formulated. Specific compounds

which have received or are currently receiving predominant consideration for aircraft fire protection applications are listed in Table 1 along with their pertinent physical and chemical properties. The relative fire extinguishing effectiveness of these agents is not included in Table 1 since effectivity of an agent will be dependent from a practical standpoint upon the type(s) of fire situations it is expected to cope with. Accordingly, the relative effectiveness of the Halon* compounds of current interest will be analyzed separately for each of the major fire problem areas previously identified.

Table 2 provides comparative threshold limit values (TLV) and emergency exposure limits (EEL) for these Halon fire extinguishants. The data was obtained from Dr. K. C. Back (1). It should be noted that for several of the Halons the TLV and EEL values are estimates which are used by the Air Force as temporary guidelines only until such time as documented values become available.

Table 3 lists the fire properties of selected Halon extinguishants. It should be recognized that certain Halon compounds can pose a fire and explosion hazard in themselves depending on the specific environmental conditions under which they are used. The hazard is of particular concern when certain agents such as Halon 1011 are utilized under high temperature or in oxygen atmosphere environments.

USE OF HALONS FOR AIRCRAFT ENGINE FIRE EXTINGUISHING SYSTEMS

A modern turbine engine installation is a maze of flammable fluid-carrying plumbing lines, and a fitting leak or rupture of these lines is almost certain to cause the flammable fluid contained therein to come in contact with likely sources of ignition such as hot bleed air lines or hot engine surfaces. More serious conditions occur from the propagation of fires resulting from malfunctioning or major failures of engines or accessories. Once started, the spread of fire is extremely rapid. Fire tests conducted by the Federal Aviation Authority (FAA) and operational experience (3) have indicated that a fire in a modern power plant can be destructive to that aircraft in a period of approximately 20 seconds. This points out the need for a fire extinguishing system in all aircraft. From a practical consideration, however, fire extinguishing systems are installed only on certain type aircraft. In military aircraft, generally speaking, single engine aircraft are not fitted with fire extinguishing systems. The philosophy being that usually an in-flight fire in the

* HALON NONENCLATURE SYSTEM -- The Halon system for naming halogenated hydrocarbons was devised by the U.S. Army Corps of Engineers to provide a convenient and quick means of reference to candidate fire extinguishing agents. The first digit in the number represents the number of carbon atoms in the compound molecule; the second digit, the number of fluorine atoms; the third digit, the number of chlorine atoms; the fourth digit, the number of bromine atoms and the fifth digit, the number of iodine atoms. Terminal zeros are dropped. Valence requirements not accounted for are assumed to be hydrogen atoms.

TABLE 1

Properties of Halogenated Hydrocarbon Fire Extinguishants

Chemical Name	Halon No.	Molecular Wt.	Freezing Point, °F	Boiling Point, °F	Critical Temp., °F	Density (LIQ) @70°F, lbs/gal	Storage Thermal Stability, °F
Carbon Tetrachloride	104	154	-9	170	341	13.[illegible]	400
Methyl Bromide	1001	95	-135	38	381	14.4	---
Bromochloromethane	1011	129	-125	153	567	16.1	250
Dibromodifluoromethane	1202	210	-223	73	390	19.0	350
Bromotrifluoromethane	1301	149	-282	-72	154	13.1	<500
1,2 Dibromotetrafluoroethane	2402	260	-167	117	418	18.0	<500
Bromochlorodifluoromethane	1211	165	-257	25	309	15.3	400
Foamed Halon*	61 wt%- Halon 1211 30 wt% - Halon 1301 Balance Additives	---	<-65	---	---	----	---

* Typical Composition

TABLE 2

Halogenated Hydrocarbon Fire Extinguishant Exposure Limits (PPM)

Compound	Threshold Limit Value (TLV)	Emergency Exposure Limit (EEL)
Carbon Tetrachloride (Halon 104)	10**	---------
Methyl Bromide (Halon 1001)	15**	---------
Bromochloromethane (Halon 1011)	200**	(10,000)
Dibromodifluoromethane (Halon 1202)	100**	(3,000)
Bromotrifluoromethane (Halon 1301)	1000**	60,000***
1,2 Dibromotetrafluoroethane (Halon 2402)	(100)	(1,000)
Bromochlorodifluoromethane (Halon 1211)	(1000)	30,000***
Foamed Halon (61% Halon 1211, 30% Halon 1301)	(No greater than Halon 1211)	---------

* Typical Candidate Composition

( )Numbers in parenthesees are unpublished values which represent estimates for use as temporary guidelines only until such time as documented values become available.

** American Conference of Governmental Industrial Hygienists (ACGIH)

*** National Academy of Science, National Research Council (NAS/NRC)

TABLE 3

Fire Properties of Halogenated Hydrocarbon Fire Extinguishants in Air and Oxygen Atmospheres (Ref 2)

Compound	Min. A.I.T.[1] of Air	Min. A.I.T.[1] of Oxygen	Flammability Limits (Volume Percent) Air L.E.L. U.E.L.	Flammability Limits (Volume Percent) Oxygen L.E.L.	Flammability Limits (Volume Percent) Oxygen U.E.L.
Halon 1011	842	694	Nonflammable @ 2-95[3]	10[4]	85[4]
Halon 1202	930	847	Nonflammable @ 5-95[3]	29[5]	80[5]
Halon 1301	<1,100[2]	1,100[2]	Nonflammable @ 10-95[3]	Nonflammable 12-98[3]	
Halon 2402	1,054	860	Nonflammable @ 6-95[3]	21[6]	52[6]
Halon 1211	<1,100[2]	1,098	Nonflammable @ 14-95[3]	Nonflammable 14-95[3]	

(1) Atmospheric pressure in a 250 cu cm glass vessel.

(2) If autoignition occurs, the AIT value is assumed to be greater than 1,100°F.

(3) Mixture temperature 450°F; Double numbers (2-95) indicate halogenated hydrocarbon percentage range over which experiments were conducted.

(4) At 212°F.

(5) At 122°F.

(6) At 212° and 450°F.

engine compartment of a single engine aircraft is associated with an engine malfunction of some type, and since the engine and its source of fuel must be shut off to obtain effective fire extinguishment, the engine should not be restarted because of the malfunction. The crew must either perform a deadstick landing or bail out. On some of our aircraft such as the B-52, KC-135, and B-47, the engines are located in pods below the wing and separated from the rest of the aircraft by a pylon. The engine compartment is isolated from the pylon with a horizontal fire-wall. These aircraft have no fire extinguishing system installed on the basis that it is improbable that a nacelle fire would be totally destructive to the aircraft. There are also other military combat aircraft which do not incorporate fire extinguishing systems on a "calculated risk' basis, but almost without exception, fire extinguishing is provided in all military transport and cargo type aircraft engine nacelles.

The requirement for an effective nacelle fire extinguishing system is based on the following considerations:

1. The selection of an effective extinguishing agent.
2. Determination of an adequate quantity of this agent.
3. Suitable equipment to store the agent until it is required.
4. Means to control the flow of the agent to the affected compartment, and distribution of the agent within the affected compartment.
5. Adequate duration of agent concentration within the compartment.

In the selection of an effective agent Table 4 illustrates the agents that have been used over the past few decades with a comparison of factors considered in choice of an agent. In regard to the effectiveness of the agents, there have been numerous laboratory tests and full scale fire tests conducted by both civil and governmental agencies that have contributed to the information available on these agents. Early testing showed that the halogenated agents were clearly superior to carbon dioxide. The reported differences in effectiveness of the various halogenated fire extinguishing agents are rather small and one must look to other properties of the agent to determine which is best for the job.

As to installed system weight, the high vapor pressure of CO_2 requires the use of high pressure containers, valves and plumbing lines, while the halogenated agents, having lower vapor pressures can be stored in lighter weight containers and they do not require high pressure tubing and valves. The relatively high densities of Halons 1011 and 1202 are advantageous from the standpoint of container charging, providing the best ratio for pounds of agent per pound of agent container weight.

Table 4 reflects the cost of the various agents in the early 1950's when the Air Force made the decision to change from CO_2 and Methyl Bromide to Halon 1011 (CB). However, cost was only a minor factor in the choice of Halon 1011. The Germans had used Halon 1011 during World War II and the agent was readily available. Effort was expended on dibromodifluoromethane (Halon 1202) in tests by the Civil Aeronautics Administration (CAA) and Aerojet-General Corporation (4). These tests proved conclusively that Halon 1202 was more effective than CB, and as

TABLE 4

Agent	Evaluated as Fire (Ref 4) Extinguisher Agent Grams*	Peak in (Ref 4) Flammability Curve Vol %	Density Lb/Gal @ 70°F	Vapor Pressure @ 130°F PSIG	1950 Cost/Lb.
Carbon Dioxide	57.94	29.5	6.34	1140	$ .05
Methyl Bromide CH_3Br	41.13	9.7	14.8	61	.30
Bromochloromethane CH_2BrCl	43.93	7.6	16.1	0	1.00
Dibromodifluoromethane CB_2F_2	39.37	4.2	19.0	25	6.00
Bromotrifluoromethane $CBrF_3$	40.57	6.1	13.1	435	6.00

* These values were obtained by calculations assuming 100 liters of gaseous mixture at 0°C and one atmosphere of pressure.

a result Halon 1212 was selected as the standard agent for fixed systems. Halon 1202 continues to be used on USAF aircraft; the C-5A being the latest aircraft exorbitant and as a result, use of Halon 1301 is planned for advanced weapon systems.

Another factor considered in the evaluation of an agent is its toxicity. The toxic properties of these agents are important; however, there is no interchange of fumes between the engine compartment and inhabited compartments of the aircraft. Exposure of maintenance personnel to the extinguishant in the case of inadvertent discharge of the system must be considered. In addition, consideration must also be given to the maintenance personnel responsible for the filling of the agent containers, since they may periodically be exposed to small concentration of agent vapors over a long period of time. The toxicity of Halon 1001 is such that other agents listed in Table 4 have not presented a toxicity problem during maintenance or charging operations.

Table 5 illustrates the two types of aircraft engine fire extinguishing systems in use and their characteristecs. The conventional and HRD systems are similar in that the agent container, discharge bonnet, direction and check valves are the same on both systems. The main difference between the two systems is their distribution system. The conventional system uses a perforated tubing arrangement for discharging the agent in the nacelle. Although the perforated tubing arrangement provides for good agent distribution, flow is restricted through the orifices and the system is heavier than the HRD system.

In contrast, the distribution in most high rate discharge systems consists of a lighter and simpler arrangement, using open-end nozzles and relying on the high velocity of the agent discharge to disperse the agent within the nacelle. High vapor pressure agents, such as Halon 1301 are more desirable for use in the HRD systems. Low vapor pressure agents like CB (Halon 1011) are best suited for use in a conventional system. Dibromodifluoromethane (Halon 1202) has been used successfully in both types of systems.

The agent quantity formulas have been derived by full scale fire tests on aircraft engine nacelles. The formulas for the high rate system are intended as a design guide with confirmation of agent concentration by the Statham Analyzer. The formula for the conventional system has a built-in margin of safety for agent quantity and this coupled with the additional lines and perforated rings makes for a weighty system. This is evident from Table 6 which compares the weight of these two types of systems on several aircraft.

Use of the Statham gas analyzer coupled with the HRD system permitted realization of a highly effective extinguishing system. The analyzer provides a means for evaluating the performance of an aircraft extinguishing system by conducting a flight test wherein the system is discharged and a continuous sampling of agent concentration can be taken and recorded on the instrument from as many as twelve different locations in the engine compartment.

TABLE 5

Aircraft Fixed Fire Extinguishing Systems

System Type	Specification	Agent	Agent Quantity	Discharge Duration	Discharge Outlets	Distr. Rqmt. Compliance
Conventional	MIL-E-5352	Bromochloromethane Dibromodifluoromethane	0.56(Wa) + (0.16) (V)*	2 Seconds or Less	Perforated Tubes	Motion Pictures
High Rate	MIL-E-22285	Bromotrifluoromethane Dibromodifluoromethane	W = 0.05V W = 0.02V+ $0.25W_a$ (Whichever is greater) Design Guide	1 Second or Less	Open Ended Lines	Agent Concentration Analyzer

* V = Net Volume of Zone in Cu. Ft.
W_a = Air Flow (Normal Cruise) in Lbs. Per Second

TABLE 6

Typical A/C Engine Fire Extinguisher Systems

Aircraft	Nacelle Net Volume Ft^3	Total Wt. of Ext. System Lbs.	Agent Halon No.	Type of System	Agent Wt./Shot Lbs.	Wt. of Agent/ Shot/Cu. Ft. (Zone)
DC-9	130*	37.1	1301	HR	8.4	.14
C5-A	557	87.2	1202	HR	7.5	.054
C-124	344	85	1011	C	19.0	.22
C-130	244	60	1011	C	13.5	.22
B-57	84	52.0	1011	C	13.5	.32
C-97	480	120	1011	C	33.0	.275
C-141	460	72	1202	HR	7.0	.06

* Includes APU

The most recent application of Halon agents concerns the use of dibromotetrafluoroethane in a pyrotechnic extinguisher wherein pyrotechnic pressurization replaces nitrogen as an energy source. Advanced aircraft operating in supersonic and hypersonic flight regimes impose many environmental problems on aircraft subsystems. Fire extinguishing equipment is no exception and standard nitrogen pressurized units could not meet the requirements over the temperature range of -65°F to 500°F. To meet this requirement, the Air Force Aero Propulsion Laboratory sponsored the development of a full-scale Pyrotechnic Gas Discharge Fire Extinguishing System with the Walter Kidde & Company (5). This pyrotechnic extinguishing system functions effectively over the -65°F to 450°F temperature range and its performance on a weight effectiveness basis is superior to that of the standard units. The USAF has had excellent experience with the various halogenated agents. A review of accidents and incidents over a six-year period (1964-1970) shows that the Halon fire extinguishing systems have been more than 90 percent effective. There are cases where we have failed to extinguish an engine fire in flight. These failures may have been due to a variety of reasons, including poor fire emergency procedures or late fire detection, with resultant severe fires incapable of being extinguished with the limited amount of agent available. This doesn't mean that aircraft have been lost because of an uncontrolled engine fire since compartmentation, isolation and combustible fluid shutoff provide additional protection.

In addition to Halons, the Air Force has considered other agents for fixed installations, namely, dry powder and liquid nitrogen. The CAA evaluated sodium bicarbonate and potassium carbonate in a series of reciprocating engine installation fire tests (3). Methyl bromide, carbon dioxide, carbon tetrachloride and mixtures were also evaluated. As a result of these tests, CAA recommended that only methyl bromide and carbon dioxide were considered satisfactory for general use in the type of engine installation tested. Advanced types of dry powder may be used for high temperature applications ($<500°F$). However, their advantages must be clearly identified to compensate for the additional cleanup problem. The FAA is evaluating the effectiveness of liquid nitrogen (LN_2) as a fire extinguishing agent for the protection of aircraft power plant installations. Preliminary test results (6) indicate the (1) LN_2 is effective in extinguishing fires in aircraft power plant compartments; (2) the quantity of LN_2 expected to be available from a LN_2 fuel tank inerting system would be sufficient to extinguish the fires; and (3) on aircraft where a large quantity of LN_2 is available, an LN_2 fire extinguisher system could provide greater in-flight power plant fire protection than the limited quantity of agent available in a conventional or high rate discharge system. Two comparative tests were conducted with Halon 1301. Although the minimum quantity of agent required for extinguishment was not determined, it is estimated that LN_2 requires approximately three to four times more agent for extinguishment as compared to Halon 1301.

The Air Force has taken the position that on aircraft equipped with LN_2 for fuel tank inerting, use of LN_2 in the engine compartment and other fire zones should be considered. However, deletion of Halon extinguishing systems will only be permitted if complete assurance exists that an adequate supply of LN_2 will be available at all times.

APPLICATION OF HALONS FOR EXPLOSION PROTECTION OF AIRCRAFT FUEL TANKS

A. Fuel Tank Inerting-Comparison of Halon 1301 and Nitrogen

Fuel tank inerting is accomplished by maintaining an adequate concentration of an inertant in the ullage throughout the entire aircraft flight profile in order to preclude the existence of flammable fuel vapor-air mixtures. This requires a continuous flow of inertant throughout the flight. The Air Force utilizes JP-4, a low flash-point fuel, for flight operations. In the case of Halon 1301, for JP-4, a concentration of 6.6 percent by volume must be present at all times to render the ullage inert. For nitrogen a sufficient quantity must be provided to limit the overall oxygen concentration below ten percent by volume. The ten volume percent oxygen limit is that required to protect against explosions initiated by high energy ignition sources such as incendiary projectiles under normal temperature and pressure environmental conditions. For point ignition sources, such as electrical sparks dilution, of the oxygen content to 12 volume percent would be adequate. For the incendiary threat the concentration requirements for Halon 1301 versus nitrogen would indicate that Halon 1301 is the preferred inertant. The selection of the preferred inertant for aircraft, however, must be based on an evaluation of a number of other relevant factors including weight penalty, fuel and fuel system compatibility, logistics, and operating costs.

Table 7 provides a comparison of Halon 1301 and nitrogen agent weights and cost penalties for a hypothetical mission profile. The inertants are compared under two methods of introduction: (1) direct or 100 percent feed of inertant into the tank throughout the mission profile and (2) premixing of the inertant with air to yield a 6.6 volume percent Halon 1301 and 52 volume percent nitrogen in air concentrations, respectively, and feeding the mixture into the fuel throughout the flight profile. For purposes of simplification the solubility of the inertants in JP-4 as well as the need for sparging dissolved oxygen from the fuel have not been considered.

Even from this simplified comparison it is immediately obvious that Halon 1301, as well as other halogenated hydrocarbons, cannot be serious contenders to nitrogen for aircraft fuel tank inerting applications. For the direct introduction method, Halon 1301 is far inferior from both weight and cost standpoints. In the case of the premixed-with-air introduction approach, Halon 1301 is attractive from a weight consideration, but is still far inferior to nitrogen from a cost standpoint.

B. Halons for Fuel Tank Explosion Suppression

In any closed vessel containing a flammable hydrocarbon fuel-air mixture there is a finite time period between ignition and attainment of destructive combustion overpressures. The specific time period is affected by the pressure and temperature of the mixture, the specific fuel/air ratio, volume of the vessel, configuration of the vessel, whether the mixture is quiescent or already turbulent when the ignition

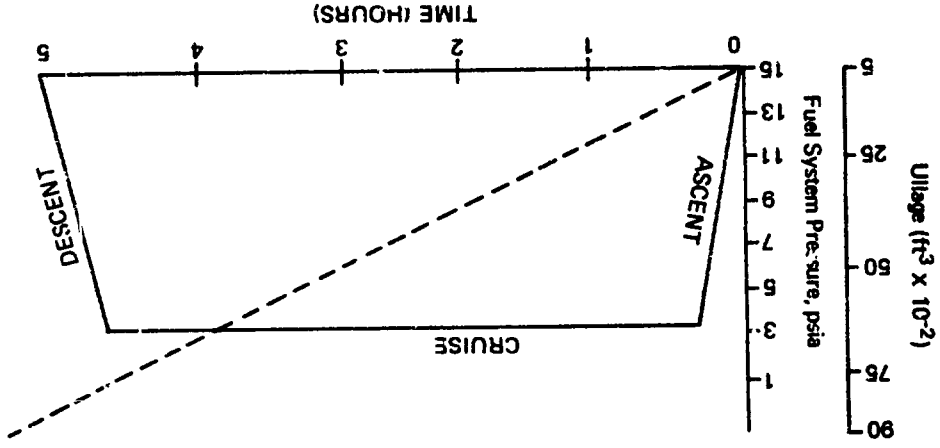
TABLE 7

Comparison of Halon 1301 and Nitrogen for Aircraft Fuel Tank Inerting

Inertant	Method of Introduction	Weight - Inertant	Cost of Inertant per Mission - $
Halon 1301	Direct	3290	3290 x $2.50 = $8225
Nitrogen	Direct	675	675 x $0.05 = $33.75
Halon	Premixed with Air	260	260 x $2.50 = $650
Nitrogen	Premixed with Air	381	381 x $0.05 = $19.05

Simplifying Assumptions:

(1) Tank Volume - 10,000 Ft^3
(2) Inertant Solubility in Fuel Ignored
(3) Temperature - 70°F (Const.)
(4) Initial Ullage - 5% or 500 Ft^3
(5) No Sparging of Dissolved Oxygen in Fuel Required



source is applied, and the type and intensity of the ignition source. Individual fuel tanks in aircraft can vary in volume from 50 to several thousand gallons, and have a wide range of configurations. Generally, aircraft fuel tanks are designed to withstand static overpressures of three to five psi. Accordingly, if a halogenated hydrocarbon extinguishant can be discharged rapidly enough and in sufficient quantity to quench the vapor phase combustion reaction before the associated overpressure exceeds three to five psi then an effective fire and explosion protection capability would exist. As most of you are aware, this technique for suppressing jet fuel-air explosions has been in existence since the mid-1950's. For point-type ignition sources in a small-volume tank (100 gal.) approximately 20-30 msec are available for detection of the ignition event, activation of the suppressor, and distribution of the suppressant. Systems are currently available which perform well within this time limit. In the case of incendiary projectiles, much more rapid flame propagation rates are experienced because of the multi-point nature of this type of ignition source and the turbulence induced by the projectile. As a result, detection and suppression of the reaction must take place within five to ten msec. Unfortunately, the rapidity of action required for the combat environment is not reliably offerred by currently available chemical extinguishant explosion suppression systems. Accordingly, this method of protection is considered inferior to nitrogen inerting and use of polyurethane flame arrestor foam for military aircraft applications. The chemical suppressant approach is attractive where the more common type ignition sources are present and for example is currently employed on some 707 jet aircraft to protect surge tanks and on the Concorde to prevent flame propagation in a fuel vent duct.

For this application, high boiling point and high density Halons are preferred to minimize canister weight and facilitate rapid explosive discharge of the suppressant. Halon 2402 possesses these desired properties and is generally proposed for explosion suppression on board aircraft. Halon 2402 also possesses good high temperature environmental stability enabling extension of its use to higher performance aircraft of Mach 2.2 and above.

The effectiveness of this type of Chemical Explosion Suppression System requires the mating of a rapid flame surveillance system with a rapidly acting suppressant dispensing capability. A system of this type results in a weight penalty of approximately 0.3 pounds per cubic foot of volume protected. Installation difficulties may be encountered for certain aircraft fuel tank applications because of internal arrangement of equipment, spars, webs and partitions. Because this system is utilized in areas on board aircraft which are remote from personnel, toxicity of the Halon suppressant is not of major concern.

FIRE EXTINGUISHING AGENTS FOR A/C HABITABLE COMPARTMENTS

Ideally for habitable compartment applications one would desire a fire extinguishing agent that is highly effective and totally nontoxic in both the neat and pyrolyzed forms. Unfortunately, the realization of this ideal situation will probably never be attainable. From

a practical standpoint, therefore, if a potentially serious fire threat exists which jeopardizes life and property, then one must select the best fire extinguishing agent and a suitable application technique from available state-of-the-art technology which can effectively counteract the threat. The selection of the "best" usually involves a number of factors other than agent fire extinguishing effectivity and toxicity, such as cost, weight, availability and dispensability. Depending on the nature of the fire threat, the type of agent, the quantity required, and the method of application will vary. For a low order fire threat, protection is provided by first aid portable fire extinguishers which are manually operated. As the magnitude of the fire threat increases a total flooding fire extinguishing system may be required. The "best" agent for these two modes of application is not necessarily the same.

A. Halon Agents for First-Aid Fire Extinguisher Applications

The habitable compartments of an Air Force aircraft are considered to be those areas which are accessible to personnel during flight. Generally, these include the cargo/passenger compartments as well as the flight deck but exclude under-the-floor cargo and accessory compartments. These latter areas may be accessible to the crew in flight but are not entered during the course of normal operations. The potential for all classes of fire is present, particularly in the case of the large cargo aircraft where a mixed cargo of personnel, fueled vehicles, baggage and freight may be encountered within one aircraft.

Effective first-aid fire extinguishment therefore requires that agents possess multi-class fire-fighting capabilities under the environmental conditions existing aboard operational aircraft. A rather high degree of effectiveness is required in order that any fire can be rapidly controlled so as to preclude the development of a catastrophic situation with respect to structural damage, levels of toxic combustion products, temperature and involvement of additional combustibles. The neat agent materials should be relatively low in toxicity, in terms of short duration exposure, and produce a minimum of vision-obscuring vapor or aerosol on discharge. The discharged agent should provide rapid knockdown and extinguishment of a fire, prevent reflash at the fire site for five minutes or more, result in a minimum of smoke and fumes consistent with the amount of agent required for extinguishment and, ideally, prevent spread of the fire to adjacent combustibles. The toxicity hazard of fire extinguishants considered for use in enclosed areas such as cabin and cargo compartments, and their degradation products must be balanced against the toxic combustion products resulting from the fire itself, most of which are of an insidious nature. In the case of many synthetic materials used or carried aboard aircraft, other toxic vapors and fumes such as hydrogen chloride, and cyanogen can result from their combustion or thermal degradation, in addition to the commonly produced carbon monoxide, carbon dioxide and water vapor. Fire retardant compounds can also contribute to the toxic species resulting from on-board fires. Successful fire control and extinguishment in any enclosed environment are dependent on early discovery, correct application of an adequate quantity of an effective extinguishant in the least amount of time required to extinguish the blaze and prevent re-ignition. Only in

this manner can the problems related to an on-board fire be reduced to the levels consistent with survival of both the aircraft and the personnel aboard.

The agent materials most commonly used by the Air Force against aircraft ground fires are not suitable for on-board fire-fighting purposes for a number of reasons. Water, although excellent against Class "A" fires, cannot be used against Class "B" or "C" fires in aircraft. Its high freezing point also negates its use in view of the Air Force's low temperature requirement of -65°F. Fire-fighting foams, both mechanical and chemical, combat Class "A" and "B" fires satisfactorily but have slow knock-down times and higher than required freeze points since all, until recently, are water-diluted. These foams are also readily blocked from reaching remote areas with restricted access. Generally none but the chemical foams are dispensed from first-aid type extinguisher equipment and the chemically-generated foams are too corrosive to the aircraft structure. The dry chemical extinguishants are quite efficient against Class "B" and "C" fires and reasonably so against Class "A" fires. However, these agents produce a rather dense cloud on release which remains suspended and therefore is vision-obscuring for an undesirably long period. The powders are also deleterious to mechanical and electronic equipment upon which they may deposit. Carbon dioxide is satisfactory as an agent against Class "B" and "C" fires but is not particularly effective for Class "A" combustibles. Reignition of a fire can occur fairly easily after extinguishment with CO_2. In confined inhabited areas, such as an aircraft cabin or cargo compartment, care must be exercised in release of an odorless agent such as CO_2 since concentrations above ten percent in air can result in unconsciousness of exposed personnel. It should be noted here that commercial passenger aircraft carry both CO_2 and water extinguishers as the fire protective devices for cabin use. The use of water is limited to Class "A" combustibles while the CO_2 units are intended for use in the galley area against both Class "B" and "C" fires or in other cabin locations with similar fire potentials. The vaporizable fire extinguishants, a family of halogenated hydrocarbons referred to as "Halons," range in character from a normally gaseous compound (Halon 1301) to materials boiling 150°F (Halon 1011), as shown earlier in Table 1. These Halons have been found to have widely varying effectiveness against all classes of fires, either in the hand portable extinguishers or in fixed system applications. All act on the fire in a chemical mode, e.g., chain-breaking and free radical reactions, as well as cooling and blanketing. All are at least three times more effective than carbon dioxide on a pound-for-pound basis against Class "B" fires. The higher boiling members approach the capability of water against Class "A" fires and all are quite efficient for Class "C" involvement. As an example, National Bureau of Standards evaluations (7) of portable extinguishers found that: "Extinguishers of the type of the one quart chlorobromomethane, ten pound carbon dioxide, and four pound dry chemical devices described herein ranked very closely with each other as useful for attack on test fires and were superior to other types of extinguishers used in this program on flammable liquid fires of limited extent." Within the Halon family there are differences in effectiveness depending on the size, type of combustible and configuration of the fire incident or test, as pointed out by Engibous and Torkelson (8) in their work for the Air Force.

The question, "Why not use the best possible agent for each fire class rather than a single agent that is not the optimum for all?" naturally arises. The Air Force faces a different situation than the airlines, who, as noted earlier, carry both CO_2 and water extinguishers in the cabin area. Air Force aircraft perform a wide variety of mission functions including troop and cargo transport. First-aid (portable) fire extinguishers must therefore be capable of performing under a variety of induced and natural environmental conditions imposed by these varied mission requirements. The required fire protection must be achieved with as little weight and volume penalty to the system as possible. While all classes of fire can occur on board military aircraft, compared to commercial aircraft there is a greater likelihood of Class "B" fires occurring in the fuselage area of military aircraft. The potentiality of fire resulting from hostile action must also be taken into account. These factors all led the then Air Corps to adopt the multi-purpose, single agent approach in 1949 with the introduction of the one quart (A-20) bromochloromethane (CB or Halon 1011) extinguisher, replacing the one-quart (A-2) carbon tetrachloride and the 4BT carbon dioxide extinguishers, for on-board fire protection. This change provided an increase in the degree of fire protection available with a reduction in weight and volume penalty, reduced toxicological hazard and reduced logistic problems. Lastly, it eliminated the necessity for crew personnel to make a choice or decision as to the correct extinguisher to use in case of an on-board fire emergency.

Several hundred thousand of the A-20 CB (Halon 1011) portable fire extinguishers have been put in service since its adoption as an AF standard item of equipment in December 1949. Over the past 22 years of world-wide use by the Air Force, some problems have been reported as would be expected. Most of these problems have centered around the toxicity of the agent Halon 1011. Isolated instances have been reported where the irritative effects of this agent have contributed directly to an aircraft accident. However, to date no deaths or serious injuries can be traced to the toxicity from the CB-filled A-20 fire extinguisher used in combatting an in-flight fire. Generally the problems recorded have been the result of mis-use of, misapplication of, or unfamiliarity with, the equipment and its contents. Detailed statistical data is not available with respect to successful useage of this equipment. A sampling of available, but incomplete, information (Tables 8 and 9) does give some indication of the frequency with which this equipment has been needed or successfully utilized.

As can be seen from these sets of data, comparatively few cabin/cockpit fires occurred in relation to the overall Air Force aircraft fire history for the period between 1964 and 1967. As shown in both Tables 8 and 9, the preponderance of cabin/cockpit fire incidents have been Class "C" (electrical) in nature. Table 9 shows the successful usage of the A-20 (Halon 1011) portable fire extinguisher in combating of A/C fires, not only in the cabin/cockpit areas on board aircraft, but also on fires external to the fuselage or cabin areas. In several cases effective use of the A-20 extinguisher by the crew was instrumental in preventing loss of the aircraft and life due to an on-board fire. No information is available as to the instances when the portable extinguishers have not been successful when properly utilized.

TABLE 8 (Ref. 9)

USAF In-Flight Fires (1965-1967)

In-flight Fires		Cabin/Cockpit Fires		
Major accidents -	99	Class "A"	1	
Minor accidents -	15	Class "C"	14	(2 major)
Incidents -	225	Total	15	
Total	339			

TABLE 9 (Ref. 10)

Recorded A-20 Extinguisher Uses (Jan. 1964 - Jun. 1965)

Cabin/Cockpit Area (Ground and Inflight)		External to Fuselage	
Cargo	2	A/C Engine (Fuel)	8
Electrical	5	A/C Brakes	1
Heater Units	1	Electrical	1
A.P.U.	1	Total	10
Total	9		

Although the overall performance record of the A-20 extinguisher with Halon 1011 has been good, there has been a continual fear in using the agent because of the toxicity hazard. As a result, in June, 1970, a program was initiated by the Air Force to provide a fire extinguishing agent which is more effective and less toxic than Halon 1011 for use in aircraft habitable compartments. The target agent was to be useable over the -65°F to +160°F temperature range, be effective against all classes of fires, be capable of preventing reignition for at least six minutes and be able to isolate adjacent combustibles from a fire area. The program was successfully carried out by Arthur D. Little, Inc. under AF Aero Propulsion Laboratory contract and resulted in the development of a foaming type of agent, based on Halon 1211, Halon 1301, and a nonionic alkanolamide surface active agent. Using the Air Force A-20 one quart extinguisher, modified to allow reasonable delivery rates of the new agent, both Class "A" and Class "B" fires were defeated over twice as effectively as with Halon 1011 from the standard A-20. Class "C" fires are difficult to standardize upon but on an electrical resistivity-conductivity basis the new agent was more than adequate. Since a minimum of agent was required to extinguish the enclosed test fires, a minimum of smoke and fumes was generated and the concentrations of toxic degradation products appeared to be within emergency exposure limits. Details of the work are contained in AFAPL TR-71-21. "Development of Halogenated Hydrocarbon Foam (Halofoam) Extinguishants," dated April 1971, and has been reported on at the annual meeting of the National

Fire Protection Association held in San Francisco in May 1971. A program is currently in progress, also by Arthur D. Little, Inc., to design and optimize fire extinguisher units, in the one quart and two gallon size, to dispense the foam-type agent in the best possible manner for on-board use in aircraft habitable compartments. A post-contract evaluation of the new agent/extinguisher unit combination will be conducted by the Air Force to verify performance and design requirements preparatory to introduction of the extinguishers and agent into the AF inventory.

B. Halon Agent Total Flooding Fire Extinguishing System for A/C Habitable and Cargo Compartments

With the introduction of large transport aircraft such as the Air Force C5A a more sophisticated fire protection capability is required to defend against the high mission impact, loss of life and monetary loss that could result from unwanted fires. Previous reliance on small portable first-aid fire extinguishers for combatting fires in habitable A/C compartments is becoming impractical because of their limited capacity and the dependence of their effectivity on rapid human response. In view of the fact that the large military transport/cargo aircraft will frequently be carrying fueled ground vehicles and a variety of other highly flammable cargo and may be exposed to a hostile (gunfire) environment, rapid fire initiation and gross fire involvement are possible. The only confident means for coping with such a gross fire problem is to provide for total flooding of the compartment with suitable fire extinguishant. The desired properties for the agent include:

(1) That it be effective at a low volume and weight percent concentrations in air for Class A, B and C fire threats. The low volume percent requirement is necessary to preclude internal overpressurization and consequent structural damage to the aircraft. Minimal agent weight concentration is desired to limit the weight penalty of the fire suppression system on overall aircraft performance (range and/or cargo and passenger carrying capacity).

(2) That it be easily and rapidly dispersable in air throughout the compartment, i.e., be a vaporizable liquid possessing a low boiling temperature (below -65°F).

(3) When uniformly dispersed in air at the effective inerting concentration, that the resulting "neat" agent vapor-air mixture be breathable for a short exposure period (several minutes) without seriously affecting personnel actions.

(4) That the toxicity hazard due to pyrolysis of the agent be the lowest possible for the class of agent being considered.

Of the Halon agents listed in Tables 1, 2 and 3 the best candidate for fulfilling the above requirements is Halon 1301. A comparison of Halon 1301 versis Halon 2402, Halon 1211 and nitrogen for the total flooding application mode in A/C habitable and cargo compartment is provided in Table 10. Nitrogen has been included because of the emphasis

being placed on its use for inerting of aircraft fuel tanks resulting in its consideration for other fire protection applications on the aircraft. The data in Table 10 is based on the respective agent concentration requirements in air to suppress and provide inerting for volatile jet fuel fires. For this purpose agent peak concentration values for n-heptane fuel were used.

Inspection of the agents included in Tables 1, 2 and 3 indicates that Halon 1301 best fulfills the overall performance requirements. Under the concentration requirements for effective total flooding fire suppression capability all candidate agents pose a hazard to personnel to some degree. In the case of the Halon agents the hazard to personnel is aggravated by their susceptibility to pyrolysis when in contact with flame or hot surfaces. The assessment of the additional hazard posed by the limited pyrolysis of the agent during the flame extinction process compared to the toxicity of the by-products generated by the unwanted fire itself is very difficult to specify other than in a qualitative manner. Recently, the Bureau of Mines in a program conducted for the Air Force Aero Propulsion Laboratory has evaluated the concentration of carbon monoxide (CO), hydrogen bromide (HB_r) and hydrogen fluoride (HF) products formed during total flooding fire suppression with Halon 1301. Tests were conducted in a 216 cubic feet chamber utilizing cotton sheeting, paper sheeting and nylon-paper sheeting as fuels. Fuel loadings were varied from 0.018 to 0.07 oz/ft^3 and fuel geometry was designed to provide for a rapid flame spread rate. In addition to varying the preburn time, the influence of final agent concentration and application rate and technique was also evaluated. As would be expected, varying the above test parameters influenced the concentration of hazardous by-products formed. Typical by-product concentrations for various combustibles and preburn times obtained in these Halon 1301 total flooding fire extinguishment tests are shown in Table 11.

These tests were primarily performed to evaluate the Halon 1301 pyrolysis threat when used in a total flooding mode in relatively small volume, 200 to 500 cubic feet, jet aircraft escape capsules. The magnitude of the pyrolysis product hazard is dependent on the type of combustible involved, the rapidity of flame spread, the duration of the fire prior to discharging the Halon 1301, and the rate and manner in which the agent is dispensed. As the volume of the compartment is increased while the initial fire involvement is kept constant, the severity of the pyrolysis product hazard decreases. Accordingly, with a sufficiently rapid response Halon 1301 total flooding fire suppression system, the agent pyrolysis and combustion products hazards for large volume compartments do not appear to pose a serious threat. Regardless of the agent utilized, whenever a fire occurs in habitable quarters on an aircraft, precautionary measures such as use of emergency breathing oxygen should be immediately taken until egress of the aircraft can be accomplished.

CONCLUSIONS

A. In evaluating the overall aircraft fire protection requirements, the extent of the measures taken are dictated by a critical as-

TABLE 10

Comparison of Selected Fire Extinguishants for Aircraft Habitable and Cargo Compartment Total Flooding Applications

Halon Nr.	Formula	Boiling Point (°F)	Mol. Wt.	Toxicity(1)	Vol. % in(2) Air @1 ATM	Wt.(3) Lbs.	Comment
1301	CF_3Br	-72	149	1	6.1	1260	Overall best, will form pyrolysis products.
1211	CF_2BrCl	25	165	2	9.3	2200	Will form pyrolysis products.
2402	CF_2BrCF_2Br	117	260	3	4.9	1750	Not readily vaporizable. Will form pyrolysis products.
Nitrogen	N_2	-320	28	Asphyxiation	43	2740	No pyrolysis problem; poses structure over-pressure problem.

(1) Relative toxicity ranking (neat agent): 1 - least toxic, 3 - most toxic.

(2) Agent peak concentration requirements for N-Heptane.

(3) Agent weight requirement for 50,000 ft.^{3} compartment at 70°F and 1 ATM pressure.

TABLE 11

Carbon Monoxide, Hydrogen Bromide and Hydrogen Fluoride Produced from Extinguishing Experiments with Six Percent Halon 1301 for the Nylon Sheeting - Paper Sheeting Combination, Paper Sheeting, and Cotton Sheeting Burning in Air in a 216 $Ft.^3$ Vessel

Combustible	Combustible Loading, Oz/Ft^3	Preburn* Time, (Secs.)	Combustible Consumed, %	CO (PPM)	HF (PPM)	HBr (PPM)
Nylon Sheeting (65%) Paper Sheeting (35%)	0.035	5	5	50	60	5
		10	24	75	130	10
		17	53	239	200	200
Paper Sheeting	0.035	3	21	100	800	190
		6	36	1000	400	22
		8	72	2000	250	25
Cotton Sheeting	0.035	5	3	600	18	1
		10	7	400	2	2
		15	13	500	13	2
		25	85	3000	60	4

*At end of preburn Halon 1301 was introduced at injection pressure of 350 psig; extinguishment time varied between 1 and 2 seconds.

sessment of the probability of a particular fire and explosion threat occurring and its effects on mission performance and loss of personnel and property.

B. A number of potential approaches for counteracting the fire and explosion threat are usually available. Selection of the best approach(es) involves an engineering evaluation of a number of factors such as aircraft operational penalties, personnel safety, compatibility with aircraft and flight environments, cost, reliability and maintenance requirements.

C. Halon fire extinguishing agents presently offer the greatest advantage for the following aircraft fire protection applications:

1. Extinguishment of engine installation fires.
2. Suppression of fuel tank explosions induced by point type ignition sources. Complexity of internal fuel tank configuration may pose an installation problem.
3. Fire suppression in large cargo and habitable compartments by means of total flooding.
4. First-aid fire extinguishers for Class A, B and C fire protection capability.

The specific halon fire extinguishing agent best suited for each of the above applications will vary.

D. Current halon fire extinguishing agents are not competitive with other available fire and explosion suppression techniques for:

1. Fuel tank inerting.
2. Suppression of explosions induced by multipoint ignition sources, such as incendiary gunfire.

E. The application of any fire extinguishing agent on-board an aircraft will require certain precautionary measures especially in habitable compartments. In general, Air Force experience with halon extinguishing agents for aircraft fire protection has been very good.

REFERENCES:

1. Private Communication - K. C. Back, 6570th Aerospace Medical Research Laboratory, Wright-Patterson AFB, January 12, 1972.

2. H. E. Perlee et al., "Flammability Characteristics of Selected Halogenated Hydrocarbons," Bureau of Mines R. I. 6748, 1966.

3. A. W. Dallas and H. I. Hansberry, "Determination of Means to Safeguard Aircraft from Powerplant Fires in Flight," CAA Technical Development Report No. 33, September, 1943.

4. "The Halogenated Extinguishing Agents," NFPA Q 48-8, October, 1954.

5. L. V. Hebenstriet et al., "Development of Full Scale Pyrotechnic Generated Gas Discharge Fire Extinguishing System," AFAPL TR 69-66, May, 1969.

6. J. E. Demaree, "Extinguishing Aircraft Powerplant Fires with Liquid Nitrogen," Data Report No. 54, FAA (NAFEC), April, 1969.

7 "Methods of Testing Small Fire Extinguishers," National Bureau of Standards Building Materials and Structures Report No. 150, June 14, 1957.

8. D. L. Engibous and T. R. Torkelson, "A Study of Vaporizable Extinguishants," WADC TR 59-463, January, 1960.

9. "Flammability in Cockpit/Cabin Environments," USAF Deputy Inspector General - Aerospace Safety Study 25-68, June, 1968.

10. NFPA-Aviation Bulletin No. 362, Appendix A, "USAF Record Use of A-20 (CB) Extinguishers," February, 1969.

11. J. M. Kuchta et al., "Ignition and Fire Suppression in Aerospace Vehicles," Air Force Aero Propulsion Laboratory Technical Report 71-93, January, 1972.

12. "Halogenated Fire Extinguishing Agent Systems (Halon 1301)," NFPA No. 12A-T Tentative, May, 1968.

REMARKS

Dr. Walter: Homer Carhart of the Naval Research Laboratory is going to tell us about experiences with halogenated agents in closed naval environments.

APPLICATIONS OF GASEOUS FIRE EXTINGUISHANTS IN SUBMARINES

Homer W. Carhart and George H. Fielding

Naval Research Laboratory

INTRODUCTION

In some of man's endeavors, he seems to be determined to encapsulate himself and then place the capsule in an exceedingly hostile environment, such as outer space or the depth of the sea. Being thus encapsulated, he now must control his atmosphere in order to make the capsule habitable for a significant period of time. Physiologically it is highly desirable (indeed, almost necessary) to keep the oxygen partial pressure at about 0.2-0.3 atm., as shown in Table 1, but the total pressure must now be adjusted to suit the mission of the capsule. Of necessity, then, the concentration of oxygen will vary widely, as can also be seen in Table 1, and from the standpoint of fire hazard, this becomes the critical factor. We all recall the disastrous fire in the Apollo capsule five years ago in which the atmosphere was 100 percent oxygen at 16 psi. By the same token, in SeaLab II, with an oxygen concentration of only four percent (the rest being predominantly He), fires could not occur. Indeed, the Aquanauts tried to smoke but could not even get a match to ignite. Submarines are designed to operate at near one atmosphere pressure, but this fluctuates, as does the oxygen concentration, depending on operating conditions.

Lest the reader think that manned capsules such as those given in Table 1 are vehicles for only the select few, let him consider the jet airplane, with its cargo of several hundred, which is also a capsule in an exceedingly hostile environment where the pressure is below that needed to sustain life, the temperature low enough to freeze him and the atmosphere going past him at 600 mph. Let him also recall that there is a mighty thin skin between him and this hostile environment, and that fires do occur in aircraft and that occasionally oxygen is used.

PHYSIOLOGICAL HAZARDS OF FIRES

It is a striking fact that, in many losses of life in fires, the actual cause of death is very difficult to identify, and usually remains unknown. This situation may be largely academic in situations where an entire structure burns, and where there are obviously several lethal effects superimposed on persons who cannot escape from the burning structure. On Naval ships at least, and especially in submarines, the situation is not academic. The basic structure cannot burn, but there is a great variety of combustion products, the identities and quantities of which depend on the combustibles available and the way

TABLE 1

Comparison of Manned Capsules

Capsule	Total Press. (atm.)	Percent Oxygen	Oxygen Partial Press. (atm.)
Apollo	0.3	100	0.3
Submarine	1.0	21	0.2
SeaLab II	7.0	4	0.3

TABLE 2

Habitability Equipment

	Number	Capacity	Removes
CO_2 Scrubber	2	250 cfm (each)	CO_2, Acids
Catalytic Burner	2	500 cfm (each)	H_2, CO, Most organics
Main Carbon Bed	1	500 lbs.	Odors, Organics, other vapors
Electrostatic Precipitators	Various	~12,000 cfm (Total)	Aerosols
Oxygen Generator	1 - 2	120 SCFH (each)	

they burn. If the principal lethal effects could be identified, steps to remove or ameliorate them could be attempted.

The effects of carbon monoxide, carbon dioxide, oxygen deficiency, hydrogen chloride, hydrogen cyanide, and nitrogen oxides are reasonably well known, and the modification of these effects by the presence of aerosols of carbon, tars and oils is beginning to be appreciated. On the other hand, the effects of heat (apart from gross burns) on the respiratory tract and body exterior are not generally realized. The same can be said of the ease with which lethal ambient temperatures can be produced, even from relatively small fires. Johnson and Ramskill have shown that the burning of two pounds of cellulose or one pint of hydrocarbon will produce an adiabatic temperature rise of about 80°C in a 6500 cu. ft. compartment (1). Normally the resultant temperature would be about the boiling point of water, and, even if the exposure were short, irreversible damage to the respiratory tract could be expected.

In reporting extensive World War II studies on the physiological effects of gasoline fires, Moritz states, "...animals as large as dogs and pigs when exposed to this kind of a conflagration for more than 30 seconds may receive injuries that are almost immediately fatal....It appeared that the rapid death may result from systemic disturbances caused by the impact of heat energy on the surface of the body." (2)

Information of this type emphasizes the importance of not merely extinguishing fires in closed manned systems such as submarines, but of extinguishing them very rapidly. Or perhaps, better yet, providing an atmosphere in which fires cannot start.

THE ATMOSPHERE IN SUBMARINES

Because of the very long submergence times of submarines, the large numbers of people aboard and the complexity of machinery and functions, it is necessary to keep regenerating the atmosphere in these vessels in order to keep them habitable. Pertinent habitability devices are shown in Table 2. These operate continuously.

Oxygen is produced at 2500-3000 psi by electrolysis of water. Of necessity this produces twice as much hydrogen at the same pressure. This high pressure allows transfer of the oxygen directly into the oxygen banks without the use of noisy compressors, and permits direct disposal of the hydrogen overboard against the sea pressure. It is easily recognized that from a fire and explosion standpoint, this can be a dangerous piece of equipment and accidents have happened. Leakage alone must be constantly guarded against - of hydrogen because it is so highly flammable, of oxygen because it enhances fires so much.

The CO_2 Scrubber is based on extraction of CO_2 from the atmosphere by a solution of monoethanolamine (MEA) from which the CO_2 is then removed by heat and pumped overboard. The regenerated MEA is then reused.

The Catalytic Burner is operated at about 600°F and is designed to burn H_2 (mostly from charging of the batteries), CO (mostly from tobacco smoking) and organics (from many sources) to CO_2 and H_2O. The catalyst is Hopcalite (mixed manganese and copper oxides) which is very effective for H_2 and CO, and, at high temperature, for most organics, but some organics, especially halogenated ones, are not completely destroyed and can generate halogen acids and other undesirable products (3, 4, 5).

The main charcoal bed is effective for removal of higher boiling organics, particularly odors, but it needs to be replenished on a periodic basis to avoid overloading the charcoal. Replenishment charcoal is carried on patrols.

There are a number of electrostatic precipitators on a submarine to remove aerosols, primarily tobacco and galley smokes. They have to be cleaned periodically.

Since the composition and pressure of the atmosphere in submarines can be varied, submariners are cautioned not to exceed 21 percent oxygen, regardless of total pressure, in order to avoid increase in fire hazards. The CO_2 content in operating nuclear submarines is normally high, averaging from 0.8-1.2 percent. From a practical standpoint this would have little significance in terms of fire. Hundreds of organic and inorganic gases and vapors have been shown to be present, many of which have been identified. These include CO, H_2 and a great variety of hydrocarbons, but, again, from a practical fire standpoint, they would have little significance because of their relatively low concentrations. However, if hydrocarbon vapors are allowed to concentrate on the carbon bed excessively, as has happened in the past, it has been shown in the laboratory that they would be a real fire and toxicity hazard should the carbon bed be ignited (6).

FIRE FIGHTING AGENTS

Several fire extinguishants are carried aboard or have been proposed. These include Halon 1310, CO_2, $KHCO_3$, Aqueous Film Forming Foam (AFFF), water and, we now also suggest N_2. Seawater mains and hoses are available, but with all the electric and electrically-powered equipment on board this is not a desirable agent. However, the use of deionized water, or a water spray (7), for local application does offer considerable appeal. AFFF (Light Water) is an excellent agent for hydrocarbon fires on a flat surface but is not much better than water for Class A or three-dimensional fires. $KHCO_3$ (P-K-P) is excellent for knocking down fires and is carried on some ships. Its main disadvantages are deposition in critical and hard-to-reach areas and obscuration. (Visibility in submarines is exceedingly important, especially while "fighting" the ship.)

Table 3 shows expected interactions of $KHCO_3$ and the gaseous agents, Halon 1301, CO_2 and N_2 with habitability equipment. As shown, Halon 1301 reacts with the carbon bed and the catalytic burner (8). Obviously CO_2 reacts with the scrubber. $KHCO_3$ would probably deposit

TABLE 3

Interaction of Habitability Equipment with Fire Fighting Agents

Equipment	Agent			
	1301	CO_2	$KHCO_3$	N_2
Carbon bed	Yes	-	?	-
Scrubber	-	Yes	Yes	-
Burner	Yes	-	?	-
Precipitator	-	-	Yes	-

TABLE 4

Limits of Flammability of Hexane or Heptane in Air Plus Added Gases

(Total Pressure of 1 Atm.)

	Nitrogen*	Carbon Dioxide*	Halon 1301**
Added Gas, %	42	29	7.2
Oxygen, %	12.1	14.9	19.4

*Data of Coward and Jones for hexane inerting (11)

**Data of NFPA 12A for heptane inerting (12)

somewhat in the charcoal bed, with little effect, and in the catalyst bed where it would decompose to the carbonate. Since ten percent Li_2CO_3 is added to the catalyst to neutralize traces of acid formed, the added K_2CO_3 would have little deleterious effect in small quantities. In the CO_2 scrubber, small amounts of $KHCO_3$ would probably dissolve in the MEA solution; if too much is scrubbed out, the MEA solution would have to be changed. Replenishment MEA is carried aboard. Release of $KHCO_3$ in the ship to fight a fire might easily overload the precipitators causing them to arc, a highly undesirable situation, since, among other things, this generates ozone.

QUANTITIES OF GASEOUS EXTINGUISHANTS

In a closed manned system, such as a submarine, one must be concerned not only with control of any fire but with potential effects of any extinguishants on the men and ship. Therefore, consideration must be given to the amounts and concentrations of extinguishants released.

The first consideration is the concentration of agent needed to prevent a fire. Table 4 gives such data which show that the order of effectiveness is: Halon 1301 > CO_2 > N_2. It is recognized that the values in Table 4 are for hydrocarbon vapors only and do not apply to all fire situations, but they will be used as being reasonable "ballpark" figures for further discussion. Using these numbers, and the concept of total flooding, one can then calculate how much agent would be needed for a given space. The "floodable" volume of a representative nuclear submarine is about 125,000 ft^3. This is divided into compartments, the smaller of the main ones being about 10,000 ft^3. Using this as a representative volume, the data in Table 5 show the weights of agent needed to protect this space from fire. The numbers are surprisingly close, but are also quite high.

The amounts in Table 5 would protect against a fire, but, if used, what about the habitability of the atmospheres they would create, i.e., what about the men? Obviously, one cannot release sufficient CO_2 to give a 29 percent concentration and expect men to live in such a space. Therefore, unless there is a very fast way to remove the agent, one must worry about the total effect in the submarine. If one can raise the concentration of agent locally enough to control a fire, how much can be tolerated once this is dispersed throughout the ship and how large a space will this amount protect? Let us assume that men can use air masks* for short term protection, at least until the agent is completely dispersed. The movement and mixing of air in a submarine is quite rapid so unless compartments are isolated, everyone in the submarine will soon be exposed.

Again it is necessary to make approximations and we will assume that the "tolerable" (certainly not healthy) concentrations of agents

*Air-line masks, supplied from the compressed air banks, are available on nuclear submarines.

TABLE 5

Quantities of Agents Required for Fire Protection Against Flammable Gases in Submarines

(Total Pressure of 1 Atm.)

Agent	Agent Conc.	10,000 ft^3 Compartment
Halon 1301 (Extinguishment)*	3.7%	140 lbs.
Halon 1301 (Inerting)*	7.2%	270 lbs.
Nitrogen (Inerting)**	42%	300 lbs.
Carbon Dioxide (Inerting)**	29%	325 lbs.

*NFPA 12A Data (12)

**Coward and Jones Data for 1 Atm total pressure (11)

TABLE 6

Portion of Ship Inertable by Amount of Agent Which is Tolerable When Present at Uniform Concentration Throughout Ship

(Total Pressure of 1 Atm.)

Agent	Assumed Tolerable Conc. (%)	Lbs. Agent Required for 125,000 ft^3	Inerting Conc. (%)	Potential Inerted Vol. (ft^3)
1301	4	1,900	7.2	69,000
CO_2	4	560	29	17,000
N_2	88	3,750	42	125,000

TABLE 7

Limits of Combustion of Solid Flammables in Air Superpressurized with Nitrogen*

Component Gas	No Combustion	Incomplete Combustion**
Air	1 ATM	1 ATM
Oxygen	0.21 ATM (6%)	0.21 ATM (13.1%)
Nitrogen superpressure	2.5 ATM (71%)	0.6 ATM (38%)
Total pressure	3.5 ATM	1.6 ATM

*Data of Cook et al. (9)
**Smoldering and Self-Extinguishment

are those listed in Table 6. These assumptions are not totally arbitrary; they do have some physiological basis. It must also be recognized that we are considering reasonably long exposures.

From Table 6 we can see the calculated weight of agent required to produce the "tolerable" concentration in a 125,000 ft^3 submarine. By using the inerting concentrations from Table 4, the potential inerted volume can be calculated. On this basis, one can arrive at a maximum potential volume of the ship that can be inerted and still stay within overall tolerable concentrations.

The data in Table 6 are given for a total pressure of one atmosphere, but release of the agents in the quantities given would also affect the total pressure. This would be particularly true for N_2 because of the way it might be employed.

NITROGEN

In Tables 4 and 6 it is seen that 42 percent added N_2 is needed for inerting. At one atmosphere total pressure this generates an atmosphere containing 12 percent O_2 (the other 88 percent being essentially N_2 as shown in Table 6) which means an oxygen partial pressure of 0.12 atm. This would be unpleasant and maybe sickening at first, but that it could be tolerated for long periods can be seen by the fact that it is about the same as the partial pressure of oxygen on Pike's Peak (14,000 ft.) and only slightly lower than that at LaPaz, Bolivia (12,000 ft.) a city of over half a million population. However, this assumes that we stay at one atmosphere pressure, but as we have implied earlier, this is not necessary in a submarine. The pressure can be increased, especially at depth. It must also be recognized that the release of any inert gas into the submarine, even in large quantities, will not affect the partial pressure of oxygen. Since the physiological requirements for oxygen depend on its partial pressure and not on the total pressure of the atmosphere, addition of even considerable quantities of nitrogen would not decrease the acceptability of the atmosphere in this regard.

Cook, et al., (9) have shown that if ordinary air is superpressurized with an additional 2.5 atm. of N_2, no combustion of paper will occur. If the superpressurizing is with only an additional 0.6 atm. of N_2, ignited paper is self-extinguishing. As seen in Table 7, this latter figure gives an atmosphere in which the concentration of oxygen is 13.1 percent which is why the fire fails to propagate, but the partial pressure of O_2 in both instances is still 0.21 atm. and, hence, acceptable physiologically. At the higher total pressure of 3.5 atm., however, the problem of decompression of the men after the event would become a factor.

It must be recognized that the figures given in Table 7 apply only to cellulosic materials, tested in a specific way, and on the authors' definitions of "no combustion" and "incomplete combustion". But, again using the "ball-park" concept, these figures do indicate that the concept of using only N_2 to superpressurize the ship should be

seriously considered as a fire fighting technique. This is particularly true since, as shown in Table 3, N_2 has no interaction with habitability equipment.

To assist in visualizing the use of the superpressurized nitrogen for inerting only, the pressurization phase could be accomplished either by: (a) simply releasing pure nitrogen gas over a period of, say 30 minutes until the total pressure reaches the desired value, say 1.6 atmospheres; (b) releasing compressed air only as fast as the crew consumes oxygen, thus building up the pressure very slowly. For extinguishment of a fire starting at 1 atm. pressure, pure nitrogen gas could be released rapidly at the site of a fire in the amount necessary to inert the local atmosphere, later allowing the added nitrogen to be mixed with the rest of the atmosphere throughout the submarine.

The concept of pressurizing a submarine is not new. In the early days of the nuclear submarines when electrolytic generators had not yet been installed, oxygen had to be carried under pressure and in the form of chemicals (chlorate candles). Towards the end of a long "dive", when the oxygen was being used up, in a few instances the submarine was occasionally pressurized somewhat with air from the high pressure banks to supply additional oxygen in order to prolong the dive. Under these conditions, the concentration of oxygen would gradually drop but a physiologically satisfactory partial pressure of oxygen could be maintained. Pressurizing a submarine also confers a small additional bonus in that this automatically permits a corresponding increase in maximum operating depth.

CARBON DIOXIDE

Table 6 shows how much total CO_2 could be "tolerated" in a 125,000 ft^3 submarine. On a weight basis, this comes to 560 lbs. Table 8 shows the rate of removal of CO_2 for a single scrubber. It is seen that at 4.0 percent CO_2, the estimated rate of removal would be 65 lbs./hr. assuming 50 percent efficiency. Nuclear submarines carry two scrubbers, so this value can be doubled. The low assumed efficiency is based not only on the efficiency of the scrubber but on the fact that the present removal system (stripper and compressor) might become too overloaded to be highly efficient. However, even at a higher efficiency the rate of removal would still be slow. At four percent CO_2 the men would undoubtedly be hyperventilating, but even under normal conditions they would still produce an additional 10-12 lbs. of CO_2/hr., which would also have to be removed.

As shown in Table 3, CO_2 does not interact with other habitability equipment, so that in limited amounts it would be quite acceptable for use in submarines.

HALON 1301

Table 6 shows that a total of 1900 lbs. of Halon 1301 could be "tolerated" in a 125,000 ft^3 submarine. Normally, it would be used in much smaller quantities, but the problem of disposal would still be very

real. As shown in Table 2, a submarine carries 500 lbs. of activated charcoal which at saturation has been found to hold over 25 percent of its weight or organic vapors. The question was raised regarding the potential of using this charcoal for adsorbing and removing any released Halon 1301. The first experiment (10) was to determine the maximum capacity for adsorption under equilibrium conditions using the pure gas only (i.e., obtain the B.E.T. isotherm). This is plotted in Figure 1 for pressures from near zero to 1 atm. (Curve B is the first part of Curve A, up to 50 mm. pressure.) It can be seen that the total amount of adsorption is low - even at 1 atm. pressure of pure Halon 1301 the charcoal adsorbs only 65 cc of halon/gram. Another interesting but not unexpected effect can also be seen in Figure 1. It is noted that the points for adsorption and desorption fall on the same curve, i.e., there is no hysteresis, showing no measurable irreversible reaction of the halon with the carbon (by this technique).

From a more practical standpoint, it is necessary to know the adsorption characteristics in a dynamic system, such as in a submarine. Figure 2 shows the results of passing air containing one percent Halon 1301 through a 10 cm. charcoal bed at 100 cm./min. (10). Curve B shows that with continuous input the charcoal bed "breaks" at about 30 min., and at about 80 min. the exit concentration is about 50 percent of the inlet concentration. It was also of interest to determine whether under flow conditions, the charcoal was behaving primarily as a pure physical

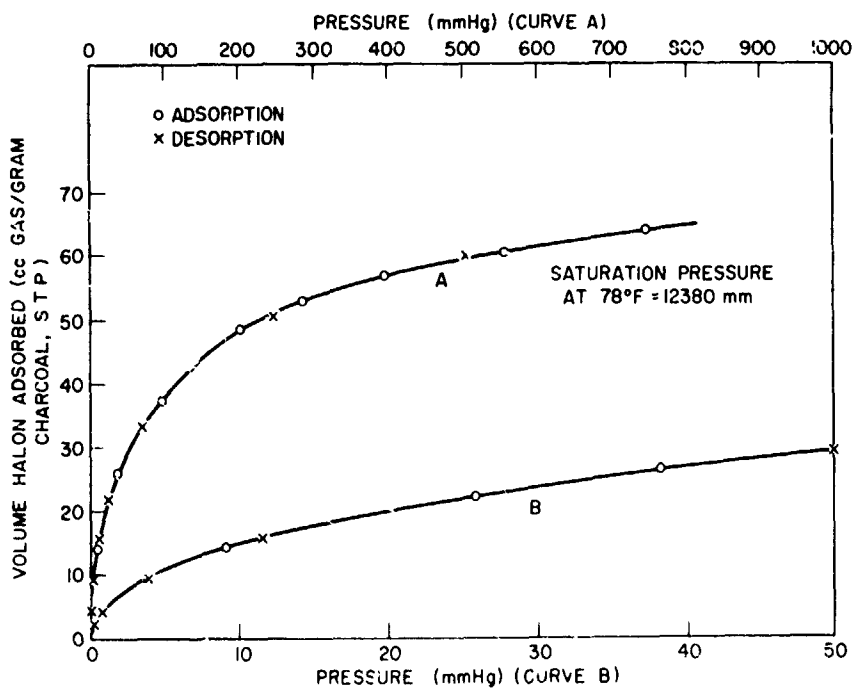


FIGURE 1. Sorption of Halon 1301 on submarine charcoal at 25.5°C (~ 78°F) (trifluorobromomethane).

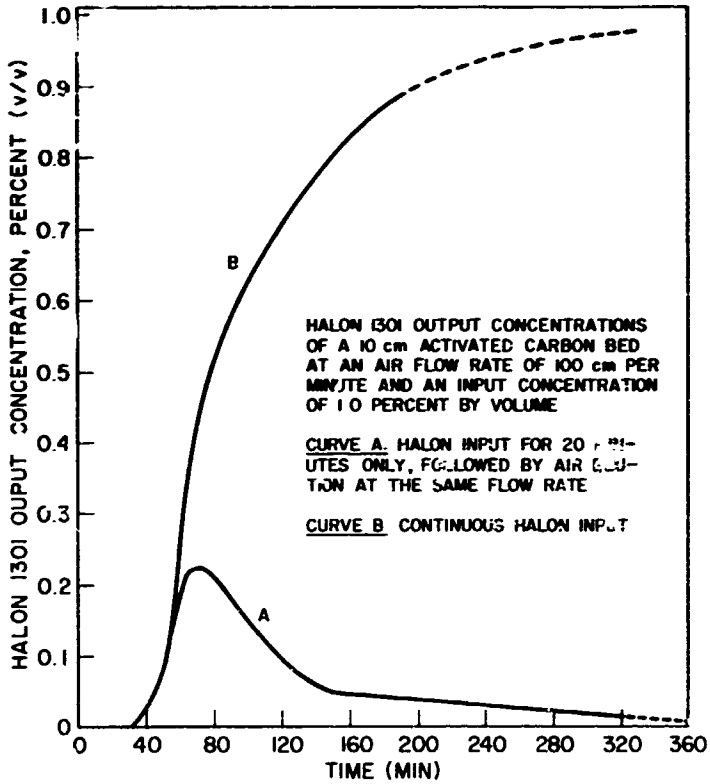


FIGURE 2. Halon 1301 output concentration, percent (v/v).

adsorbent (in which case it would perform like a chromatographic column), so, after 20 min. flow of one percent halon, only air was passed through the bed. As seen by Curve A, the "break" occurred right on schedule (30 min.) and a chromatographic type elution peak resulted. This shows that the retention is essentially pure physical adsorption.

From results such as those presented in Figures 1 and 2, one can determine the amounts of Halon 1301 removed from an air stream (i.e., retained on the charcoal) for different flow rates, concentrations, and "break-times". Table 9 shows examples of such data for two flow rates, three concentrations and two definitions of "break-time," 10 ppm and 10 percent of input found in the effluent. Extrapolation of the data in Table 9 yields the numbers presented in Table 10. The airflow rate of 2860 cm./min. (94 fpm) is representative of that in a submarine. Under these conditions the pitifully small amount of only about 10 lbs. of Halon 1301 would be removed by a 500 lb. bed of charcoal, up to 10 percent "break-point." If the charcoal were not removed, even this would eventually be eluted back into the ship to an equilibrium concentration.

Since the charcoal bed would not be an effective removal device, halon released into the submarine would remain for a long time unless it interacted with other systems. As shown in Table 3, it does react with the catalytic burner. Compounds containing C, H and O only are burned "clean" (i.e., to CO_2 and H_2O) in the burner, but compounds con-

TABLE 8

Typical Performance of a Single CO_2 Scrubber in Submarines; Air Flow of 15000 cfh

Input Conc., Percent	Output Conc., Percent	Total CO_2 in Ship, lbs.	CO_2 Removed/hr., lbs.	Efficiency, Percent
0.8	0.32	112	8	60
1.0	0.29	140	12	71
1.5	0.54	210	16	64
2.5	1.2*	350	40*	50
4.0	2.0*	560	65*	50

*These data based on an estimated scrubber efficiency of 50 percent; no performance data available.

TABLE 9

Adsorption of Halon 1301 on Activated Charcoal
Laboratory Data

Air Flow Rate, cm./min.	Halon Conc. in Air, percent	Break Time, min. (10 ppm)	Halon on Char at Break, cc	Break Time, min. (10% of input)	Halon on Char at Break, cc
100	0.085	70	6.0	107	8.9
100	1.0	30	30	48	47
100	13	5	65	12	113
1000	1.0	0.9	9.0	2.6	25

*Coconut shell charcoal, 4.5 grams, bed depth of 10.2 cm. (4.0 in.)

TABLE 10

Adsorption of Halon 1301 on Activated Charcoal
Scale-up of Data

Air Flow Rate, cm./min.	Halon Con. in Air, percent	Break Time min. (10% of input)	Halon on Char at Break cc/g. of char	Halon on 500 lbs. char at Break, lbs.
100	1.0	48	10	33
1000	1.0	2.6	5	16.5
2860	1.0	-	-	~10*

*10 lbs. Halon 1301 vapor = 38 cu. ft. at 25°C; volume at 4% vapor conc. = 950 cu. ft.

TABLE 11

Thermal Decomposition of Halons on Hopcalite* Catalyst (4,8)

Halon No.	Refrigerant No.	Structural Formula	Vapor Conc. (ppm)	Decomposition (%) 305°C	360°C
1220	R-12	CCl_2F_2	420-440	0	0
2420	R-114	$CClF_2$-$CClF_2$	85-410	-	0
1130	R-11	CCl_3F	30-100	17	37
1301	R-13B1	$CBrF_3$	100-600	ca. 0.2**	ca. 3
2402	R-114B2	$CBrF_2$-$CBrF_2$	100	30	-

*Hopcalite: 85.0% MnO_2; 14.2% CuO

**315°C

NOTE: Data from NRL Report 6546 and Memo Report 2189

taining halogens may or may not generate halogen acids, depending on how stable they are. Table 11 gives data on the stability of several of these, including Halon 1301 (4,8). (R-11, 12 and 114 are used extensively as refrigerants on board, but, because of the instability of R-11, it is being supplanted by R-114.) As Table 11 shows, Halon 1301 decomposes only about 0.2 percent per pass at the nominal operating temperature of the burner of 315°C. But temperature cycling and uneven heating found in operating burners lead to "hot spots" at temperatures even in excess of 360°C where the decomposition is about three percent per pass. At the quantities of halon needed to fight a fire, this represents the generation of a considerable amount of halogen acids, a situation that would soon become intolerable, and the burner would have to be shut off.

CONCLUSIONS

From the above, it would appear that Halon 1301 could be quite effective, but if it is used, it would eventually be necessary to surface and ventilate the ship. In certain cases this might be considered as aborting the required secrecy of some patrols. In wartime, surfacing, even to snorkel depth, could be disastrous. It is recognized that a major fire constitutes an emergency, however, and the chance may have to be taken. If practiced, the half-life for removal of a contaminant by snorkeling is about one half hour.

CO_2 could be used for small fires, (i.e., the more common ones) but not for "flooding" the ship unless the men donned their air masks and the ship ventilated. At low total usage, the CO_2 could probably be handled without ventilating.

Nitrogen, though a relatively poor fire fighting agent, offers some very interesting possibilities by just allowing it to pressurize the submarine as it is released. Return to a "normal" atmosphere after a fire would be relatively easy. Oxygen from the banks (or generator) could be added at such a rate that approximately 0.21 atmosphere partial pressure of oxygen could be maintained while the overpressure is being reduced by pumping the "vitiated" air back into selected banks for disposal later. Thus, return to "normal" could be accomplished without the need for ventilating.

REFERENCES:

1. J. E. Johnson and E. A. Ramskill, "Fire and Noxious Gases: Effect on Internal Environments of Protective Shelters," in Protective Structures for Civilian Populations, NAS/NRC Symposium, April, 1965.

2. A. R. Moritz, "Physiological Mechanisms Concerned in the Production of Casualties by Exposure to Heat," Chapter 17 in War Chemistry, Parts 1-2, NDRC Summary Technical Report, Division 9, Vol. 1, 1946.

3. J. G. Christian and J.E. Johnson, "Catalytic Combustion of Nuclear Submarine Atmospheric Contaminants," NRL Report 6040, March 26, 1964.

4. J. E. Johnson and J. K. Musick, "Studies of Halogenated Hydrocarbons, Part I - Stability of Fluorocarbons in Air on Hopcalite Catalyst or Stainless Steel," NRL Report 6546, May 26, 1967.

5. J. E. Johnson and R. H. Gammon, "Halogenated Hydrocarbons, Part 2 - Decomposition of Selected Chlorinated Hydrocarbons on Hopcalite Catalyst," NRL Report 6582, July 20, 1967.

6. F. J. Woods and J. E. Johnson, "The Ignition and Combustion Properties of Activated Carbon Containing Adsorbed Hydrocarbons," NRL Report 6090, July 28, 1964.

7. A. W. Bertschy, A. F. Armington, H. E. Moran and R. L. Tuve, "A Portable Water-Spray Fire Extinguisher for Submarine Use," NRL Report 4363, June 8, 1954.

8. J. K. Musick, "The Catalytic Decomposition of the Fire Extinguishant Bromotrifluoromethane, $CBrF_3$," NRL Memorandum Report 2189, November, 1970.

9. G. A. Cook, R. E. Meirer and B. M. Shields, "Screening of Flame-Resistant Materials and Comparison of Helium with Nitrogen for Use in Diving Atmospheres," First Annual Summary Report on Combustion Safety in Diving Atmospheres," NTIS No. AD-651583, March 31, 1967.

10. J. K. Thompson and H. G. Eaton, unpublished NRL data, 1972.

11. H. F. Coward and G. W. Jones, "Limits of Flammability of Gases and Vapors," U. S. Bureau of Mines Bulletin 503, 1952.

12. Fire Protection Handbook, 13th ed., National Fire Protection Association, 1969.

REMARKS

Dr. Walter: Our next paper will be by J. M. Kuchta, who is replacing David Burgess, of the Bureau of Mines, on the "Effectiveness of Halogenated Agents Against Gaseous Explosions and Propellant Fires."

EFFECTIVENESS OF HALOGENATED AGENTS AGAINST GASEOUS EXPLOSIONS AND PROPELLANT FIRES

Joseph M. Kuchta and David Burgess

Bureau of Mines

ABSTRACT

Results were summarized from Bureau of Mines studies on the effectiveness of halogenated agents as fire and explosion suppressants and on the limitations of a commercial Halon 1301 extinguisher for use as an ignition-quenching device. Halons containing bromine tend to be more effective than those without bromine in inerting hydrocarbon-air mixtures; the Halon 1301 requirement for inerting methane-air mixtures was greater than that reported in NFPA literature. Methane-air ignitions in the Bureau's Experimental Mine were quenched by a commercial Halon 1301 extinguisher (four ft. away) only when the agent was applied before the fireball diameter exceeded some critical value ($\sim$18 inches). Dispersion experiments revealed that extinguishment failures in the mine tests were attributable to nonuniform agent distribution which resulted in the formation of voids with very low agent concentrations. A practicable concentration of Halon 1301 (e.g. 10 percent) can inert a small spill of a propellant such as Aerozine-50 at room temperature against ordinary ignition sources. However, impracticably high halon concentrations would be required to extinguish an established Aerozine-50 pool fire or to inert the maximum vapor concentrations of this propellant possible in a closed chamber.

INTRODUCTION

Halogenated hydrocarbons such as Halon 1301 (CF_3Br) are known to be highly effective in quenching the flames of hydrocarbon fuels in air. They are therefore used in fire or explosion suppression systems, although it is necessary to initially determine the design requirements for the intended application. This paper compares the inerting effectiveness of Halons 1202, 1211 and 1301 with methane-air mixtures and the results of large-scale experiments that were performed in the Bureau's Experimental Mine to evaluate a commercial Halon 1301 extinguisher. Results of dispersion experiments are also presented to explain the limitations of the extinguisher as a quenching device. In addition, data are given on the Halon 1301 requirements for inerting the vapors of hydrazine-type propellants and for extinguishing fires involving such propellants. Some attention is given to extinguishment of secondary fires and to the products of combustion of a hydrazine fuel blend (Aerozine 50) in a halon-containing atmosphere.

INERTING OF FLAMMABLE ATMOSPHERES

The efficacy of any extinguishant as an inerting agent or explosion suppressant is normally defined by the minimum concentration required to prevent flame propagation through the flammable mixtures that can be formed with a particular fuel and oxidant. This critical concentration tends to be higher for the premixed flames than for diffusion flames and, therefore, the premixed flame data should be relied upon for inerting a flammable atmosphere. Data for diffusion-type flames are applicable primarily to the extinguishment of liquid fuel fires, which will be discussed in another section of this paper.

Vaporizable halogenated hydrocarbons represent one class of extinguishants that are superior to the inert gases in suppressing gaseous explosions. Halon 1301 (CF_3Br) is perhaps the most widely used halogenated extinguishant because of its high vapor pressure, low toxicity (undecomposed), and great effectiveness as a flame inhibitor. However, exposure to the decomposition products of any halon must be avoided because of the toxicity hazard. Figure 1 shows the complete range of flammable compositions that may exist at 75°F for methane-air mixtures inhibited with

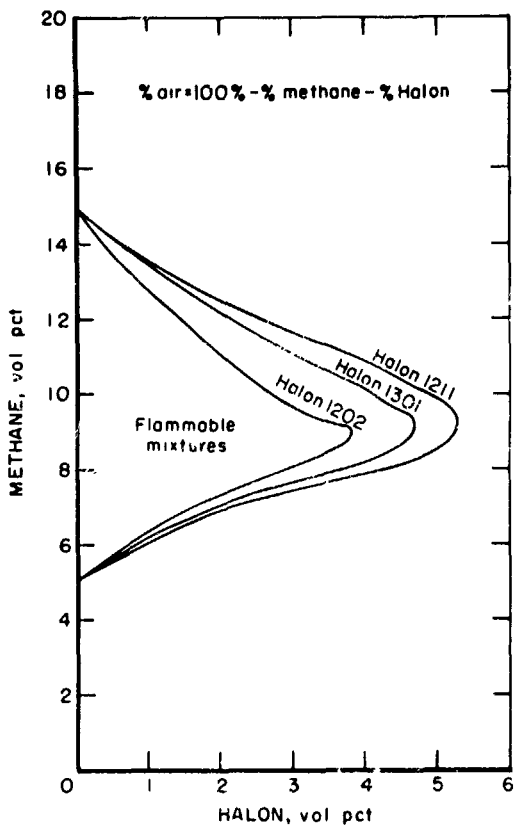


FIGURE 1. Limits of flammability of methane-air mixtures inhibited with Halons 1202, 1211 and 1301 at 75°F and atmospheric pressure (4 inch diameter tube).

this halon and with Halons 1202 (CF_2Br_2) and 1211 (CF_2BrCl). These data were obtained in the Bureau of Mines F-11 apparatus (1) (four-inch diameter by 40 inches long) under near-stagnant flow conditions; the mixtures were ignited with a spark energy source near the bottom of the tube length. At these conditions, the minimum extinguishant concentrations (volume-percent) above which flame propagations were not possible were as follows: 3.8 percent Halon 1202, 4.7 percent Halon 1301, and 5.8 percent Halon 1211. The observed value for Halon 1301 is more conservative than the 2.0 percent concentration that is specified by the NFPA (2) as adequate for inerting these mixtures; differences in apparatus dimensions could account for the data variations. It is not surprising that the halon (1202) containing the most bromine atoms was the most effective inhibitor since burning velocities are depressed more by bromide additives than by chlorides or fluorides. In comparison, an inert gas such as nitrogen has a rather small effect on flame properties; thus, at least 38 percent added nitrogen is necessary for inerting methane-air mixtures.

Generally, the flammable vapor-air mixtures of saturated hydrocarbons require less than 10 volume-percent Halon 1301 for inerting at 70°F and atmospheric pressure. (2,3) However, at least 20 percent appears to be needed for a fuel like hydrogen. Other halogenated agents which contain only fluorine and chlorine are usually much less effective than those with bromine. Figure 2 (4) shows that the inerting concentrations for gasoline vapor-air mixtures were above 10 percent with such agents as Halon 112 ($CHCl_2F$), 113 (CCl_3F) and 122 (CCl_2F_2). Note also that inerting effectiveness increases with the number of halogen atoms in these materials. Nevertheless, each of these halons was more effective than nitrogen, carbon dioxide, and the exhaust gas (gasoline engine) used in the flammability experiments. The ability of the inert gases to quench flames is largely dependent upon their capacity to absorb heat; the results for the inert gases in Figure 2 are consistent in this respect.

The inerting requirements can increase with increasing temperature since the halons are combustibles and may autoignite if sufficiently heated. Table 1 lists the minimum autoignition temperatures found for five halons in air using a 250-cc heated flask. (5) Limit-of-flammability data are also included in this table to show that three of the halons were capable of propagating flame in oxygen but not in air at the given mixture temperatures. Halon 1011, which was the only nonfluorinated agent, was the easiest to autoignite and had the widest flammability limits in oxygen.

EXPLOSION SUPPRESSION BY TOTAL FLOODING MODE

In the practical case of explosion suppression, the suppression device must detect and quench a developing flame before it propagates beyond the protected area or before the pressures become excessive. Normally, the extinguishant is discharged by the total flooding mode to provide rapid distribution of the agent. However, in a large confined space containing a flammable atmosphere, quenching of an expanding flame can be difficult to achieve if the flame has grown to some sizable fire-

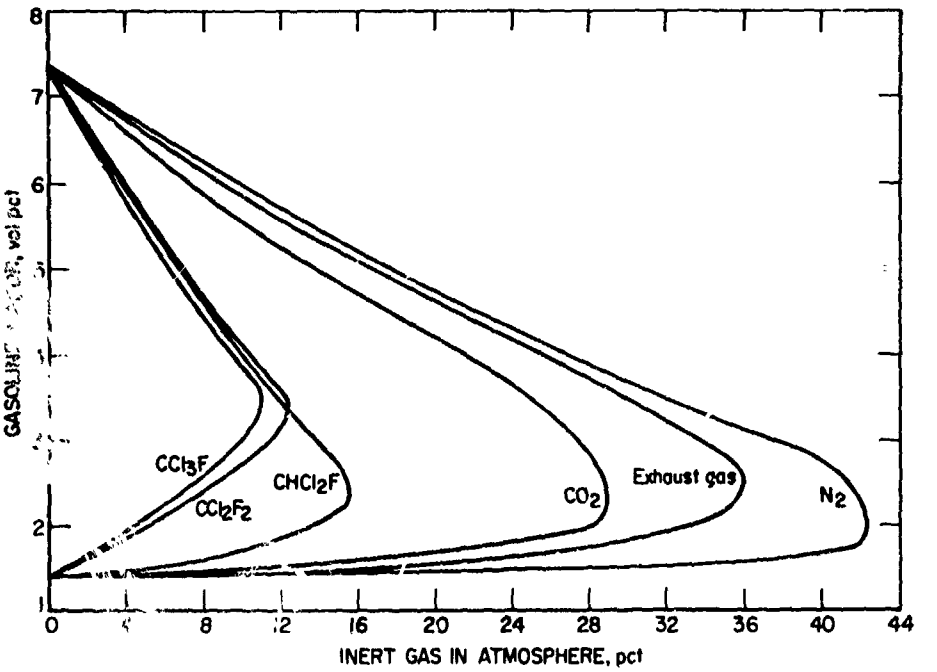


FIGURE 2. Limits of flammability of gasoline vapor in air with various inert gases and halogenated hydrocarbons at 80°F and atmospheric pressure.

ball before dispersion of the agent. This was experienced in a series of extinguishing tests (6) that were conducted in the Bureau's Experimental Mine using a commercial Halon 1301 extinguisher (Fenwal bottle).* The extinguisher was equipped with an explosively actuated diaphragm for releasing the halon through a three-inch-diameter outlet fitted with a 120° dispersion nozzle. The tests were made in a six-ft.-high by nine-ft.-wide by 24-ft.-long section of the mine entry that was filled with a stoichiometric methane-air mixture and with the extinguisher 38 inches from the point of ignition; ignition was effected by an electrical spark source which was located 10 inches from the coal face at the end of the entry.

The results from the mine tests (Table 2) showed that with about 26 lbs. of Halon 1301, effective quenching could be obtained when the halon discharge was delayed as long as 88 milliseconds but not when the delay was 97 or 123 milliseconds. Motion picture records indicated that the growth of the fireball diameter was at a rate of about 200 inches/second and that the largest diameter of flame that was extinguished was not over 18 inches. With eight-lb. Halon 1301, flame quenching was not obtained when the extinguisher delay was increased from 51 to 80 milliseconds. These records also revealed that the high turbulence produced by the discharge of extinguishant tends to make extinguishment more difficult since parts of the fireball are distended and blown away from the axis of discharge. Aside from using multiple

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

TABLE 1

Minimum Autoignition Temperatures and Limits of Flammability of Various Halogenated Hydrocarbons in Air or Oxygen

Material	Minimum AIT in air, °F	Limits of flammability* Air vol. %	Oxygen vol. %
Halon 1301 (CF_3Br)	>1100	NF (75°F)	NF (75°F)
Halon 1211 (CF_2BrCl)	>1100	NF (75°F)	NF (75°F)
Halon 2402 ($C_2F_4Br_2$)	1054	NF (212°F)	21-52 (212°F)
Halon 1202 (CF_2Br_2)	930	NF (122°F)	29-80 (122°F)
Halon 1011 (CH_2BrCl)	842	NF (212°F)	10-85 (212°F)

* NF indicates nonflammable over the range of mixture compositions investigated.

TABLE 2

Results of Flame-Quenching Tests with Halon 1301 and Stoichiometric Methane-Air Mixtures (Distance Between Extinguisher and Ignition Source - 38 inches)

Weight of Halon, lb.	Time from ignition to Halon discharge, msec.	Flame diameter at discharge time, inches	Test Result
26	38	7.6*	Quench
21	41	6	Quench
29	51	10	Quench
29	70	14*	Quench
24	80	15.8	Quench
29.5	88	17.3	Quench
26	97	19.4*	Explosion
26	123	24.5	Explosion
8	51	10.2*	Quench
8	80	16.7	Explosion

*Calculated value based on fireball growth rate of 200 in./sec.

suppression units, it was apparent that changes in the design of the extinguisher nozzle were required to provide more uniform and effective dispersion of the agent.

The dispersion pattern produced by an extinguishing system is important in determining its limitations in protecting a given area. Such information (6) was obtained for the commercial Halon 1301 extinguisher in a simulated mine entry in which the spatial and temporal distributions of the halon were determined under loading conditions similar to those used in the mine tests. The dispersion pattern that can be expected with this extinguisher is illustrated in Figure 3 in which selected frames from motion picture records show the side and rear views of the halon cloud formed after discharge. The most interesting aspect of these records is that the lateral dispersion (see rear view) is not uniform and is characterized by the existence of six or more lobes of opaque white cloud which advance laterally at a rate of about 125 ft./sec.; the frontal lobe, which is seen in the side view, advanced at a rate of 200 to 300 ft./sec. Although the lobes eventually merge, voids apparently exist in the halon cloud during the critical period (initial 100 ms.), when an explosion suppression device would be required to quench an ignition. Figures 4 and 5 show the position of the leading edge of the opaque cloud as a function of time. It is noteworthy that regardless of the loading, the extinguishant reached a point 38 inches from the nozzle within 13 milliseconds; this point corresponded to the location of the spark ignition source in the mine experiments.

Concentrations were measured in the above experiments with probes that were located in the vertical plane, 38 inches from the dispersion nozzle. Table 3 summarizes the peak Halon 1301 concentrations obtained at various probe positions. Highest concentrations were found near the axis of flow where they reached near maximum values (>20 percent) within about 50 milliseconds. At other probe positions, the halon concentration rose at slower rates and did not peak until about 100 milliseconds or more. Of particular interest are tests 2 and 3, in which the peak concentrations at probe positions 6, 7 or 8 were as low as two percent (test 2) or seven percent (test 3); furthermore, halon was not detected or was present only in small concentrations at these positions during the initial 100-millisecond period. Thus, the presence of such a "hole" in the dispersion pattern would allow a flame to continue to burn until extinguishant was brought to this position by convection. Such dispersion patterns can account for the extinguishment failures that were experienced in the mine experiments.

Presently the Bureau is investigating other nozzle dispersion designs that would improve the effectiveness of explosion suppression devices, particularly for use in quenching mine gas ignitions. For this application, it appears desirable to reduce the axial velocity of dispersion and to increase the agent concentration at the periphery of the discharge. Solid cone and hollow cone dispersion nozzles have been designed with this in mind but have not been evaluated in extinguishing tests The use of a hot propellant gas for vaporizing and dispersing the agent is also under consideration. This type of dispersal system is reported to reduce the agent concentration requirements and could be used with gaseous and liquid extinguishants.

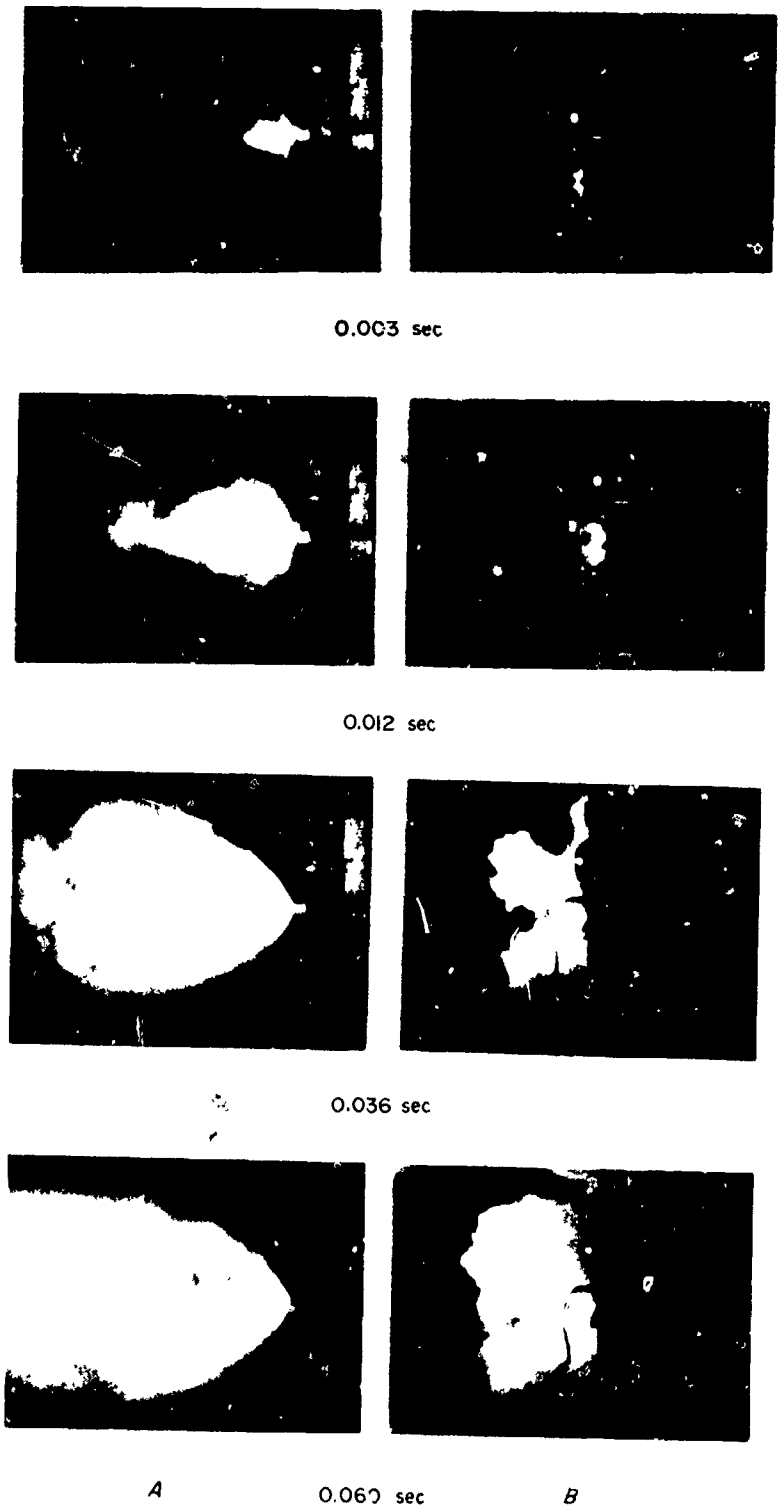


FIGURE 3. Selected frames from motion picture sequence showing (A) side view and (B) rear view of Halon 1301 stream.

TABLE 3

Summary of Peak Halon 1301 Concentrations in Dispersion Experiments with a Commercial Extinguisher

Probe Position	Distance from Axis of Flow, inches			Maximum Halon 1301 Percentages			
	Horizontal	Vertical	Radial	Test 2* 25 lb.	Test 3 25 lb.	Test 4 25 lb.	Test 5 40 lb.
1	0	-12	12	100	75	59	34
2	1.5	0	1.5	74	57	62	100
3	3.0	12	12	41	23	21	22
4	4.5	-30	30	27	15	11	16
6	25.5	-12	28	4	11	13	10
7	27.0	0	27	2	7	12	-
8	28.5	12	31	10	7**	16	12
9	48.0	-12	49	23	13	-	-
10	49.5	0	50	13	5**	9**	-
11	51.0	12	52	8	9	5	7**

*Without metal screen in extinguisher nozzle.
**Halon 1301 maximum concentration achieved only after 0.5- to 1.0-sec. delay.

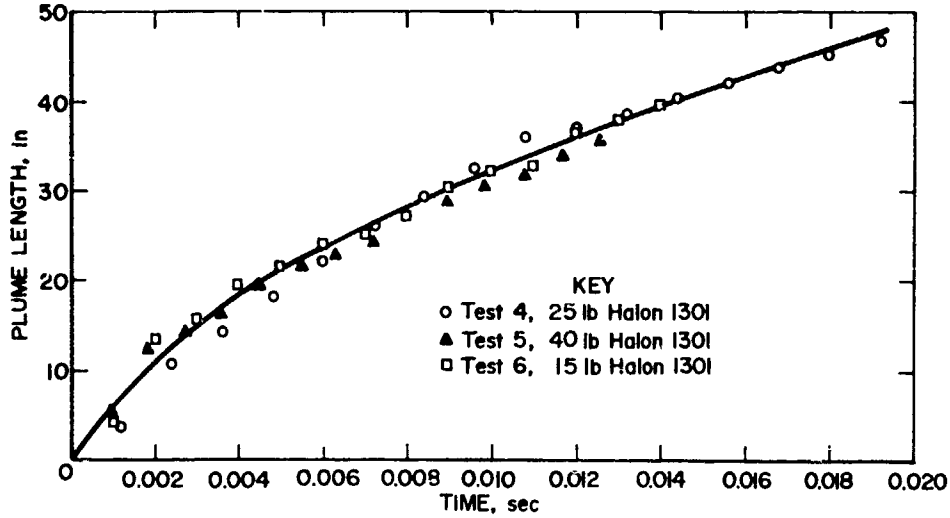


FIGURE 4. Location of leading edge of extinguishant cloud (frontal lobe as seen in side view).

APPLICATION OF HALON 1301 TO THE FLAMMABILITY HAZARDS OF AEROZINE-50

The propellant Aerozine-50 (A-50) contains by specification (7) approximately 51 wt % of hydrazine (N_2H_4) and at least 47 wt % unsymmetrical dimethylhydrazine (UDMH). Being a blend of volatile fuel (UDMH) with an endothermic one, A-50 combines the handling hazards of low flash point and wide flammable range.

In most circumstances the preferred countermeasure to a spill of A-50 is the application of copious amounts of water, because water's mutual solubility with A-50 results in a strong suppression of the fuel's vapor pressure. However, A-50 is used under some circumstances wherein a water deluge could be more damaging than the small fire that it was meant to avert. Therefore, the use of Halon 1301 as a first-stage inerting or extinguishing agent (to be followed only if necessary by water deluge) has been studied. (8) Halon "inerts" an A-50 vapor/air mixture by raising the lower flammability limit of the fuel vapor, and it inerts a pool of spilled A-50 by raising its fire point; its action in the extinguishment of a burning A-50 pool is more complicated, as will be discussed below.

The effects of Halon 1301 on the flammabilities of three representative fuel vapors in air were investigated: UDMH in concentrations from 0 to 20 percent; 80 UDMH-20 N_2H_4 from 0 to 27 percent; and 50 UDMH-50 N_2H_4 from 0 to 13 percent. These were metered as liquids through motor-driven syringes and were completely vaporized at slightly elevated temperature, typically 100°F, into a metered gas stream of air and Halon. Limits-of-flammability of the mixtures were determined in the Bureau of Mines F-11 flow apparatus.

Figure 6 shows the limit curves as determined by some 70 trials; the experimental points are omitted for clarity. A curve for 80 UDMH-20 N_2H_4/air/N_2 is included for comparison. The solid portions of the

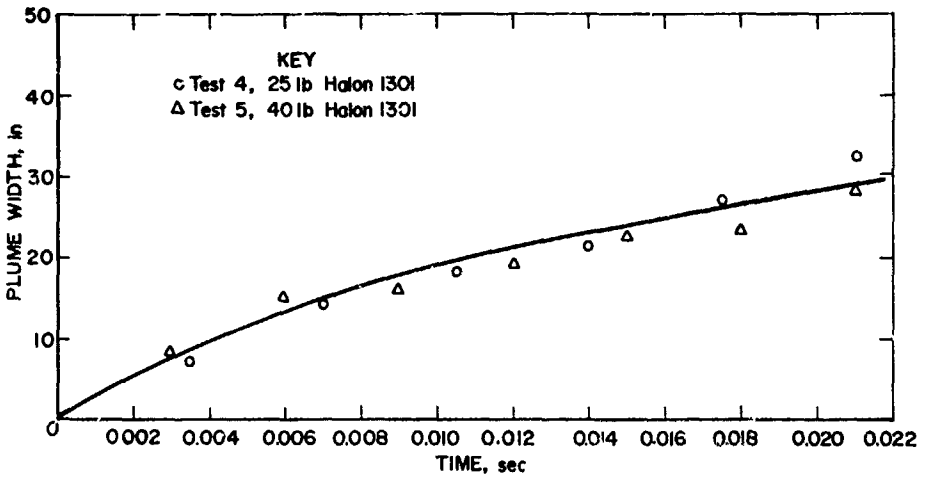


FIGURE 5. Location of leading edge of extinguishant cloud (lateral lobe as seen in rear view).

curves are terminated where the fuel vapor concentration reaches its equilibrium value at 77°F. Arrows indicate the concentrations for stoichiometric combustion to CO_2, H_2O and N_2.

The greater effectiveness of Halon 1301 as compared to N_2 appears more significant if one considers that the most probable mixtures at any distance from a spill will be lean mixtures. Nearly 60 percent of N_2 is required to inert even a very lean (80 UDMH-20 N_2H_4)/air mixture; almost the same figure has also been found for UDMH/air. (9) On the other hand, the required concentration of added halon rises much less steeply to about 20 percent at the respective concentrations for stoichiometric burning. A disappointing feature of inhibition by halon is the continued rise in requirement as the mixtures become progressively richer than stoichiometric.

The vapors from an A-50 spill become easier to inert with halon as the liquid evaporates; this follows both from the curves of Figure 6 and from the decreasing vapor pressure as UDMH is depleted in the liquid.

The inerting of A-50 pools by Halon 1301 was tested in the two-ft.-diameter by four-ft.-high chamber of Figure 7. The desired ambient atmosphere was obtained by a constant throughput of ~6.2 ft.^{3}/min. of air plus extinguishant, which entered the chamber through the diffuser coil and pebble bed at the bottom. Windows (for photographic coverage), thermocouples (for flame sensing), and a ring probe (for gas sampling) were provided. The liquid sample, initially 50 ml of A-50, was contained in a four-in.-diameter by 3/8-in.-deep crystallizing dish seated on a load cell for recording of weight loss. Ignition was effected by a spark 0.25 in. above the liquid surface. With no halon in the atmosphere at room temperature, ignition was effected reliably with each spark. Upon addition of halon, the vapors above the liquid continued to flash with each spark but pool ignition became erratic; at 6-7 percent of halon, the pool failed to ignite even with repeated sparks.

Figure 6 showed that seven percent of Halon 1301 raises the lower flammability limit of UDMH only from 2.0 to 2.7 percent. In view of this small change of flammability, the inerting by six to seven percent of halon was at first taken to be an artifact of the pool and igniter geometry. Accordingly, the work was expanded as shown in Table 4 to investigate the effects of several system parameters. Series 1 and 2 of Table 4 show that the depth of dish is relatively unimportant, whereas series 3 and 4 show the very minor effect of dish diameter. All data show that the required concentration of halon is roughly proportional to the vapor pressure of A-50.

The burning of a pool of liquid A-50 is typical of liquid pool fires except for the endothermic nature of the propellants. Figure 8 shows the radiation level (assuming spherical symmetry) and the weight loss vs. time of 90 lb. of A-50 burning in a 48-in.-diameter aluminum tray. There are clearly two stages: in the first stage, comprising about half the total weight of fuel, the burning rate is comparable to that of pure UDMH in the same diameter of pool; in the second stage, burning is faster and is accompanied by vigorous agitation of the liquid.

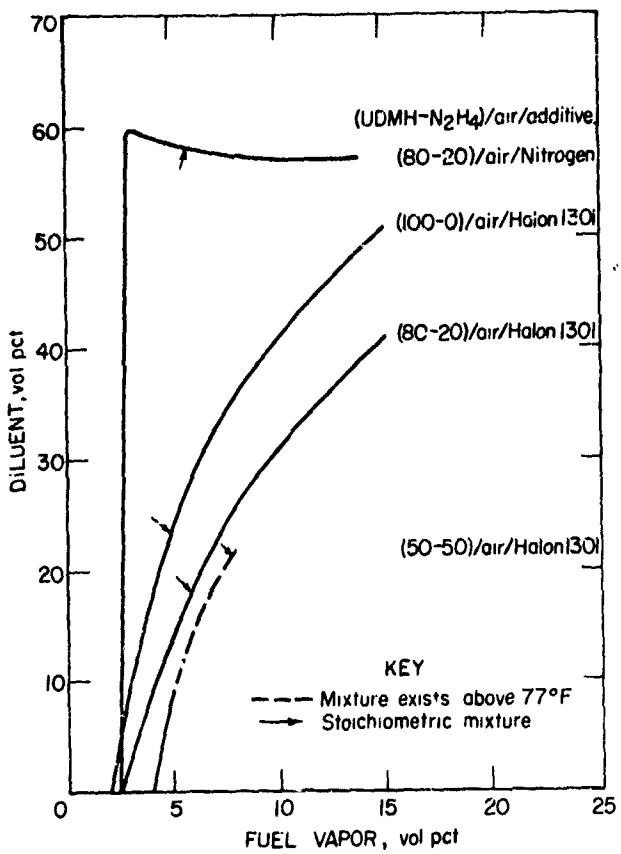


FIGURE 6. Effect of diluents on flammable limits of A-50 vapors in air at 100°F, 1 Atm.

TABLE 4

Marginal Halon 1301 Concentrations to Prevent Ignition of A-50 Pools

Series	Tray diam., in.	Tray depth, in.	Liquid temp., °F	Vapor pressure,[a] psi	Halon in air,[b] %
1 (spark)	4	0.38	57	1.6	4.9 - 7.5
2 (spark)	4	2	57	1.6	5.5 - 8.2
3 (spark)	4	0.38	84	3.0	9.3 - 11.8
4[c] (spark)	14	5	86	3.2	5.7 - 12.5
(fuse powder)					12.5
5[d] (flame)	6	0.38	72	2.2	6.3
			76	2.5	6.3

(a) Titan II Storable Propellant Handbook, AFBSO-TR-62-2, Bell Aerosystems Co., Buffalo, N. Y.

(b) I ition occurs below this range; no ignition above it.

(c) The several tests of this series were carried out in a 12-ft.-diameter sphere using 1 pint (473 ml) of A-50.

(d) Using 250 ml of A-50.

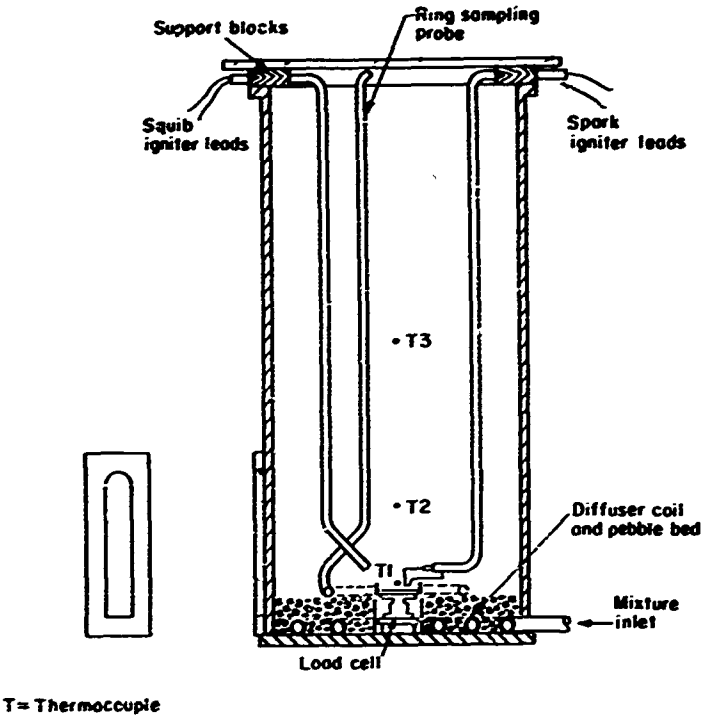


FIGURE 7. Two-foot-diameter by four-foot-long chamber used for extinguishing and igniting trials.

No effective countermeasure was found for the second stage of burning except for dilution with water. However, the fire can be extinguished during the first stage by large concentrations of CO_2 or halon.

The addition of CO_2 to the ambient air has almost no effect on the burning rate until, at 35 percent of CO_2, a UDMH or (first stage) A-50 flame abruptly blows off. The effect of adding Halon 1301 is more complicated. At some concentration in the range of 5-15 percent of Halon 1301, the luminous diffusion flame disappears and the halon then reacts directly with the hot vapors above the liquid surface, generating a dense white smoke. In the meantime, the weight loss rate is unaffected as shown in Figure 9, and burning proceeds into the usual second stage. The concentration of halon required to extinguish completely an A-50 fire is a strong function of tray diameter; thus 36 percent of Halon 1301 suffices for a four-in. tray, but 48 percent was required by a six-in.-diameter pool. Since even 36 percent is an impracticable quantity of extinguishant, the work was not pursued with larger pool diameters or depths.

In experiments similar to those on the extinguishment of A-50, conventional liquid fuels were ignited in six-in.-diameter trays, allowed a minute of burning, and then extinguished with Halon 1301. The required concentrations of Halon 1301 were five percent to extinguish burning hexane and nine percent to extinguish methanol. The similarity of these numbers to the 6.3 percent required to inert an A-50 pool and

to the 5-25 percent required to extinguish the visible flame of A-50 leads us to the following speculation: in both early and later stages of A-50 burning there is a decomposition flame close to the liquid surface with CH_4, H_2, and NH_3 as major products, followed by an air-supported diffusion flame that burns these products to CO_2, H_2O, and N_2; and the decomposition flame (at least in the early stages) is only initiated by the diffusion flame. Therefore, the inerting of an A-50 pool is comparable to the inerting of other liquid fuels; but once ignited, the A-50 fire is nearly independent of its ambient atmosphere and becomes more self-sufficient as the fuel becomes richer in N_2H_4.

Several small (three-cm.-diam.) dishfuls of A-50 were allowed to burn within a glass chamber to permit total collection of products. The smokes generated in Halon 1301 air atmospheres were caught on glass cloth filters and submitted to analysis for C, H, N, F, and Br (Table 5). The numbers have been normalized to 14.01 for nitrogen to show at a glance the degree to which the smoke is represented by its major constituent, NH_4Br. The first four columns of data refer to the early stages of A-50 burning in which the major fuel constituent was UDMH. The average empirical formula of product is $NH_{3.98}Br_{0.90}C_{0.01}F_{0.02}$. X-ray diffraction showed the samples to be impure ammonium bromide which became quite pure NH_4Br on a single recrystallization from ethyl alcohol. The final column represents a late stage burning in which the fuel would have been primarily N_2H_4. A substantial amount of fluoride appears in the smoke analysis.

The table also includes the production rates of smoke in several experiments. Smoke outputs were roughly proportional to Halon 1301 con-

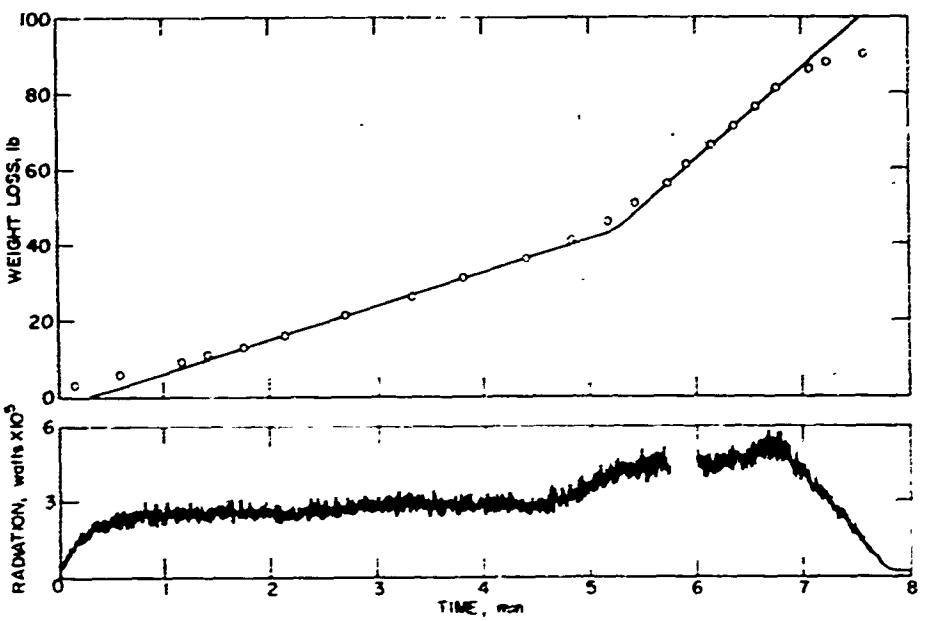


FIGURE 8. Burning of 90 pounds of A-50 from a 4-foot-diameter aluminum tray in air.

TABLE 5

Analyses of Smokes from Initial and Final Stages of Burning of A-50 Pool Fires in Contact with Various Percentages of Halon 1301

Burning Stage	1	1	1	1	2
Halon 1301, %	14.9	25.4	25.4	33.8	14.9
Smoke composition, wt fraction					
Carbon	0.21	0.05	0.06	0.17	0.10
Hydrogen	3.93	3.94	4.06	(5.08)	3.86
Nitrogen	14.0	14.0	14.0	14.0	14.0
Fluorine	0.29	0.22	0.31	0.40	1.78
Bromine	73.2	73.5	67.7	72.2	66.0
Fuel consumption, mg/sec	44	51	--	50	--
NH_4Br production, mg/sec	3.5	6.4	--	7.2	--

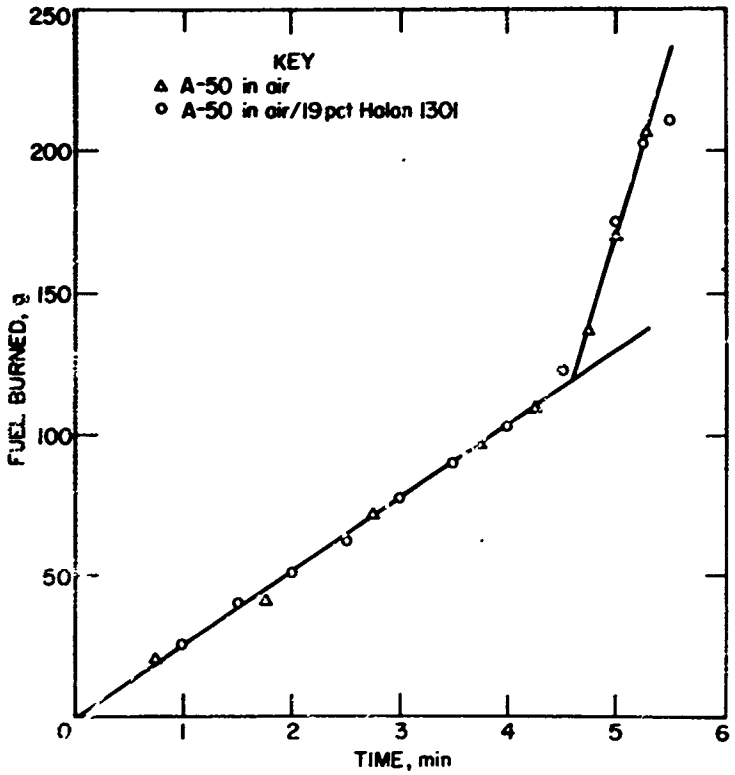


FIGURE 9. Burning of A-50 from a 6-inch-diameter glass tray, with and without Halon 1301 extinguishant.

centration. About three to six percent of the nitrogen from the burned fuel and about the same proportion of bromine from the halon appear in the NH_4Br. No appreciable smoke was found in premixed vapor/air/halon flames or in pool burnings wherein the luminous reaction zone had not been eliminated. High densities of smoke appeared during attempted spark ignitions of A-50 pools inerted by halon.

The gaseous products of the small pool fires were submitted to gas chromatography in which, unfortunately, no peak representing a fluorine compound could be identified. Table 6 shows identifiable gaseous products. In the absence of Halon 1301 (col. 2) the only gases are air, H_2O, CO_2, and excess N_2. In the halon experiments, H_2 and hydrocarbons appear in the UDMH stage of burning (col. 3), whereas NH_3 and additional H_2 appear in the N_2H_4 burning stage (col. 6). Note particularly that the same products appear at 0.6 cm. (cols. 4 and 5) from the liquid surface as 15 cm. downstream. Now consider that the burning rate from Figure 9 is completely independent of the presence of 19 percent of halon. Thus, it appears that the burning rate in each stage of burning is independent of the diffusional flame that converts intermediate products to CO_2 and H_2O. In the N_2H_4 stage (cols. 5 and 6), such intermediate products as NH_3 and H_2 are sufficiently exothermic relative to N_2H_4 to maintain a decomposition flame, but in the UDMH stage (cols. 3 and 4), much of the exothermicity depends on a small amount of H_2O that is formed near the liquid surface. Presumably this is the burning that can be inhibited by a large concentration of Halon 1301.

TABLE 6

Gaseous Products Above 3-cm-diam A-50 Pool

Burning Stage	1	1	1	2	2
Halon 1301, percent	0	25	25	25	15
Height above liquid, cm	15	15	0.6	0.6	15
Gaseous products, percent					
H_2	0.1	3.5	8.8	18.8	12.4
O_2	17.5	16.7	13.4	3.7	8.5
N_2	80.1	66.2	61.1	41.9	48.3
CH_4	--	4.1	5.2	8.5	0.2
CO	--	0.2	0.4	0.3	--
CO_2	1.8	0.1	0.1	0.0	--
C_2H_4	--	0.2	0.3	0.3	--
C_2H_6	--	0.3	0.3	0.4	--
H_2O	0.5	1.2	1.4	0.4	0.3
NH_3	--	--	0.8	17.6	27.0
Halon 1301	--	6.9	7.7	6.1	2.3
Unidentified	--	0.6	0.5	2.0	1.0

TABLE 7

Summary of Halon 1301 Requirements

Function	% Halon 1301 needed
Extinguish A-50 pool fire in air	~48*
Inert richest possible vapor-air mixture at 72°F	40-50
Inert stoichiometric vapor-air	~20
Inert A-50 pool (4-14 in. diam):	
At 85°F	9.3-11.8
At 72°F	~7
At 57°F	5.5-7.5
Destabilize premixed (Bunsen) flame	~3
Extinguish secondary fires in air:	
Methyl alcohol	9
Hexane	5
Fabrics and mylar	2**

*First stage; probably impossible to extinguish second stage.

**Reference 8.

A summary of Halon 1301 requirements is given in Table 7.

REFERENCES:

1. M. G. Zabetakis, G. S. Scott, and G. W. Jones, "Limits of Flammability of Paraffin Hydrocarbons in Air," Ind. Eng. Chem., Vol 42, 2120 (1951).

2. National Fire Protection Association, "Halogenated Extinguishing Agent Systems - Halon 1301," NFPA No. 12A, Boston, Mass., 1971, 70 pp.

3. J. E. Malcolm, "Vaporizing Fire Extinguishing Agents," Interim Report 1177, Army Corps of Engineers, Engineer Research and Development Laboratories, Fort Belvoir, Va., 1950, 91 pp.

4. H. F. Coward and G. W. Jones, "Limits of Flammability of Gases and Vapors," BuMines Bulletin 503, 1952, 155 pp.

5. H. E. Perlee, G. H. Martindill, and M. G. Zabetakis, "Flammability Characteristics of Selected Halogenated Hydrocarbons," BuMines Rept. of Inv. 6748, 1966, 12 pp.

6. D. S. Burgess, W. F. Donaldson, A. L. Furno, J. M. Kuchta, and C. R. Summers, "Spatial and Temporal Distributions of Halon 1301 from a Commercial Extinguisher," BuMines Rept. of Inv. 7515, 1971, 17 pp.

7. Amendment 2, dated February 4, 1964, to Military Specification MIL-P-27402 (USAF) dated August 25, 1961.

8. D. S. Burgess, et al., "Inerting and Extinguishment of Aerozine-50 with Water and/or CF_3Br," J. Spacecraft and Rockets, Vol 6, No. 11, November, 1969, pp. 1259-1268.

9. E. L. Litchfield and A. L. Furno, "Flammability of Propellant Combinations," Annual Report 1, August 1964-June 1965, Government Order H-76708, prepared for George C. Marshall Space Flight Center, NASA, Huntsville, Ala.

REMARKS

Dr. Christian: I have been asked a number of times since yesterday about the availability of the papers from this symposium, so I thought I ought to repeat that the Academy will assemble all of the papers into a publication, and distribute them to all of the people who have been registered at this meeting.

I am guilty of an omission. I should have mentioned earlier the fact that the fire equipment manufacturers, through their trade association, the Fire Equipment Manufacturers Association, have generously contributed financial support for the publication of these papers from the symposium. We are very grateful to them for doing that.

We have had a little slippage of the program. Some of the things ran overtime this morning, and we have banished Chairman Walter from the podium for letting that happen. This afternoon we are going to pick up what was left over from this morning's session on Applications, but we will have a new chairman, who is well qualified to handle this, because he is a retired Army man.

I am not going to try to tell you what the new program schedule is going to be like. I am not sure myself. But as we go along, the new chairman will keep you posted.

I would like to introduce to you at this time the chairman of this afternoon's session, Mr. James W. Kerr, who is among other things in charge of the fire research activities for the Office of Civil Defense. He is also a member of the Committee on Fire Research.

Mr. Kerr: Thank you, Bill. Welcome to what is left of Session III. We will talk about Session IV shortly.

The first afternoon paper today will be on Halon 1211 by Albert Edmonds, Imperial Chemical Industries, Ltd.

USE OF HALON 1211 IN HAND EXTINGUISHERS AND LOCAL APPLICATION SYSTEMS

Albert Edmonds

Imperial Chemical Industries, Ltd., England

Amongst many other activities, Mond Division of Imperial Chemical Industries is engaged in the manufacture of fire-fighting chemicals. For many years we have supplied sodium bicarbonate as the main ingredient for dry chemical formulations. In the early 1960's Halon 1211, which is widely known in the UK and other countries as BCF, was introduced. This is a liquefied gas extinguishing agent of particular value in situations where cleanliness and freedom from residues are important. The main usage of BCF is in portable extinguishers, and models of various sizes are offered by manufacturers in Britain and several other countries throughout the world, but presently excluding the USA. There now exists, however, a tentative NFPA Standard and the Underwriters' Laboratories have agreed to rate and list 1211 hand portables.

This paper is concerned with fire applications where 1211 can be used with safety and where its properties make it the preferred agent.

Mond Division developed 1211 in the belief that it would be a safer and more effective agent than carbon tetrachloride which was then in common use, but which has since been banned for fire fighting in the USA, Europe and several other countries.

In the Wright report, published in 1960, it states 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 in selecting the agent which reduces the total hazard most." How does 1211 meet these requirements?

1211 is particularly suitable for Class B and C fires and combines the special merits of high efficiency with relatively low toxicity and absence of corrosive effects. Its boiling point, -4°C (25°F), confers additional advantages in that it is low enough to give rapid volatalization and quick action on a fire, but high enough to give only a moderate vapor pressure at normal temperatures.

1211 is selected for those situations where the mess from powder or foam is unacceptable or where the fire is obscured. In the UK major outlets for 1211 extinguishers are (1) public service vehicles, (2) military vehicles, (3) laboratories, (4) telephone exchanges, (5) electric and diesel locomotives.

We have carried out a series of experiments to measure the concentration of 1211 likely to result from the discharge of hand appliances in confined spaces. It was clearly impracticable to cover every possible application by specific experiments and the following confined volumes were selected as being representative of a wide range of practical fire applications:

1. A partly ventilated room of 2,500 cu. ft. volume.

2. A well sealed room of 945 cu. ft.

3. A cab of an Austin diesel truck of estimated volume 97 cu. ft.

In several of the experiments a nominal three pound extinguisher was used, which, in most instances, would represent in practical terms an excessive use of 1211 in the smaller volumes.

The results showed that the highest concentration of 1211 always occurs at floor level and the lowest concentration at ceiling height. A "layering" effect was obtained in the well sealed room (945 cu. ft.). This condition is not observed in "total flooding" or local application systems where the energy at discharge is considerably greater and the consequent atmospheric turbulence more pronounced than that created by the discharge of a hand extinguisher.

No high local concentrations of 1211 were recorded and, as would be expected, a small degree of ventilation caused a rapid decrease in concentration at all points.

In the case of the truck, a three pound 1211 extinguisher was totally discharged into the cab through a slightly open passenger's door which was shut after discharge. The concentration of 1211 at nose height at the end of discharge was 2 percent falling to 1.3 percent after one minute.

The results obtained in the well sealed room of 945 cu. ft. capacity showed that the concentration of 1211 at nose height at the end of discharge of a three pound extinguisher was only 0.4 percent.

The overall conclusion from this work is that even in confined spaces the concentration of 1211 produced by the deliberate or accidental discharge of a hand extinguisher of a size usually provided is not hazardous.

We have now had over ten years experience in the use of 1211 hand extinguishers and this has confirmed the effectiveness, high chemical stability, and low risk of the agent.

1211 aerosol type extinguishers have fulfilled a need for a cheap, but effective appliance that would appeal to the private car owner. Because 1211 is chemically stable and has a low vapour pressure it can be stored in an aerosol for a number of years without deterioration.

Tinplate or aluminium monobloc cans are used, but the valve must have a discharge rate of 30 to 40 grams a second. The aerosol type extinguisher is a useful supplement to the standard type extinguisher in offices, laboratories and on pleasure craft. The "self evident" method of operation is a real benefit when the appliance is used, as it nearly always is, by inexperienced people.

In a well designed hand extinguisher the 1211 will be discharged as a broken liquid stream with a "throw" of between six and ten feet. The total discharge time will be in the range 10 to 18 seconds. 1211 extinguishes a fire by chemically interfering with the chain reactions taking place in the flames and to do this some decomposition occurs, the extent of which depends on the size of the fire and the time taken to extinguish it. The decomposition products consist essentially of the halogen acids which are extremely irritating to the eyes, nose and throat, even at concentrations as low as 20 ppm. The fire fighter is compelled to leave the area because of discomfort and so doing removes himself from the less obvious hazards such as carbon monoxide, hot air, and the decomposition products arising from the flammable material itself. Whatever agent is used on a fire it is good practice to ventilate the area after extinguishment. In our research laboratories at Runcorn we have a number of small fires each month and over 80 percent of these are extinguished with 1211. The laboratories are also equipped with water and dry chemical extinguishers.

Local Application Systems are covered by the Tentative NFPA Standard 12B and are defined as fire situations where the hazard is not enclosed or where the enclosure does not conform to the requirements of total flooding. Examples of hazards that have been successfully protected by local application systems in the UK are: engine compartment of military vehicles, aircraft engines, paint spray booths, floating roof oil storage tanks, and the engine compartment of power boats.

During the past three years our research team has been engaged in establishing the design data for total flood situations which, in part, has been linked with the preparation of the Standard 12B. The local applications section of the Standard is not so well documented as that on total flooding and we intend to carry out experimental work this year that will expand our knowledge on this subject and enable us to give greater guidance to fire equipment manufacturers. The impartant factors in the design of local application systems are:

1. Rate of flow

2. Limitation of nozzles

3. Quantity of 1211 required

4. Distribution system.

There will be an increasing demand for systems of this type within industry because computerized plants will not have people available to use hand extinguishers and it will be necessary to protect vulnerable parts of the plant by automatic means.

The Standard 12B permits the use of 1211 for "total flooding" applications in places which are not normally occupied, e.g., transformer bays, switch houses, pumping rooms, cable trays and tunnels. There are many such installations in Europe.

It is necessary to balance the hazards, which several of the previous speakers have spoken about, against the effectiveness of the halogenated hydrocarbons in extinguishing fires. Dr. Clark has told you about the detailed study we have made on the toxicology of 1211 and those of us who are engaged in marketing or development activities at Mond have had regular discussions with his department so that we know the problems and can give guidance to our customers on the safe usage of the product. All the Fire Equipment Manufacturers in the UK who take 1211 and National and Governmental Authorities such as The Factory Inspectorate and the Department of the Environment have been given the results of our toxicological work.

Perhaps the most important contribution we can make is the ten-year record of the safe usage of 1211 in a wide variety of industries. There are now well over a million three-pound 1211 extinguishers installed in the UK. The film which you will now see illustrates some of the applications for which 1211 has been chosen as the most appropriate agent. (Mr. Edmonds presented a film.)

REMARKS

Mr. Kerr: You may have thought that was the last paper from this morning, and in a sense it was, but actually Richard Roberts is here to report on or actually present a translation of a paper by M. Languille, of Rhone-Progil in France, on the "Applications of Halon 1211 in Fixed Systems in Normally Occupied Area."

APPLICATIONS OF HALON 1211 FIXED SYSTEMS IN NORMALLY OCCUPIED AREA

E. Languille

Presented by Richard B. Roberts, Rhodia, Inc.

Mr. Languille was planning to be here for the presentation of this paper. He has asked me to thank Dr. Walter and the Committee for the opportunity to transmit this information to you.

I was to read his paper, but only because his English would be more difficult to understand. Now as I look forward to the question period, you can be sure that I regret his absence even more than he does.

Halon 1211 is a fire extinguishing agent whose physical form is that of a liquefied gas with low vapor pressure. At atmospheric pressure it is a liquid up to 25°F. Its liquid density is 1.83 (kg/liter). These two characteristics (low vapor pressure and high density) combined with its effectiveness mean that H[illegible]211 does not require heavy walled construction either for portable u[illegible] for storage in fixed systems. The resultant savings in both weight [illegible] expense of the storage and delivery system, compared to Halon 1301 for example, are substantial. These property differences also allow better direction or "carry" of the stream for local extinction.

Rhone-Progil is one of the important manufacturers of Halon 1211 for fire extinguishing. The name of this company probably means little to most here, so a sentence or two of description is appropriate. Some of you may be more familiar with the name Pechiney connected with Halon 1211, however after various consolidations the new name is Rhone-Progil. Rhone-Progil is a part of Rhone Poulenc, one of the world's very large chemical companies with sales over two billion dollars.

Another important division of Rhone Poulenc has been a leader, over the years, in the development and manufacture of prescription pharmaceuticals. So the effect of chemicals on humans is not a new concern for us.

In the twelve years since carbon tetrachloride was banned as a fire extinguishing material in France, Rhone-Progil has developed the use of Halon 1211 including its use in fixed systems in normally occupied areas; and it has been accepted for such use by the Public Health authorities there. The professional standards of these authorities are

high. For those who have not been involved in international science, I will cite one example: a drug which proved to have serious side effects for the human embryo reached the market in the United States and in Germany; it was quickly withdrawn. But it had never been given approval in France.

Approval of Halon 1211 was given subsequent to the examination of all the toxicological studies of the product including the work of Engibous and Torkelson and the study by Professor Truhaud of the Faculty of Pharmacology in Paris. I won't dwell on this point as Dr. Back (Aeromedical Research Laboratories, USAF) mentioned yesterday, toxicity is not really an issue here. Halon 1211 has relatively low toxicity. The issue is at what level of concentration does hazard begin. I'd like to return briefly to this point in a few minutes.

First let's consider the subject of concentration level required to extinguish -- with Halon 1211. Work on this subject in France has resulted in considerably lower values than those reported in the NFPA 12B standard. These tests done by Rhone-Progil, the Fire Laboratory, and several extinguisher manufacturers all conclude that concentration levels one to two percent points lower will extinguish the same flammable liquids, vapors and gases. For most of these products to allow a margin of safety, Rhone-Progil recommends a concentration level in the protected area of three to four volume percent.

The other key parameters in Halon 1211 systems are the time to extinguish, and the rate of release. The optimal ranges for all these parameters have been found to be: a concentration level of three to four percent, a time to extinguish of two to four seconds and correspondingly a Halon 1211 release rate of one to two kilograms per minute per cubic meter. To extinguish quickly with minimum concentration, the system must be designed to deliver this kind of substantial release rate.

Designs for use in normally occupied areas should also include alarm systems to signal release. The alarm should be automatic with manual back-up. Audible alarms should be complemented with visual signs at entry ways. Exits should be clear for prompt evacuation of personnel. (In some installations this may involve a release delay of several seconds, certainly not to exceed thirty seconds.) Systems should provide for rapid ventilation of the room after the fire has been extinguished. Until this ventilation has occurred, personnel should be trained to enter only with self-contained breathing apparatus.

Now let me list some of the systems installed in France in normally occupied areas:

These include bank vaults (including safe deposit areas), electrostatic paint booths, cellulose acetate warehouses, turbine rooms, paint spraying rooms, solvent filling rooms, electric generator rooms, and electric transformer rooms. To date there have been no accidents from these installations, even though a number have already been in operation.

Understandably then, Rhone-Progil find that the NFPA limitation to normally unoccupied areas is not justified and should be lifted.

Having both lower material and hardware costs, Halon 1211 offers lower system costs and thus the possibility of more widespread use to protect people and property.

There ends the formal part of these remarks.

It is all very well to say that this NFPA limit should be lifted, but it was placed there in the first place for a reason. Their committee is composed of responsible men who acted on the available evidence.

Well, it turns out that one of the most important pieces of evidence that made them place this limitation was the toxicological work on humans which Dr. Clark from ICI reported to you yesterday.

I would be remiss and a poor representative for Rhone-Progil if I did not here take issue with some important aspects of that ICI work.

In particular we believe that the test lacked the calibration necessary to be a definitive test. As you heard in the question from the floor yesterday: no determination was made of the "no effect" concentration level for the three human subjects tested. In addition, consider the fact which you heard in Dr. Reinhardt's (du Pont) paper, that in a test chamber it took a concentration of seven percent of Halon 1301 to produce the first slight effects in humans while the mask technique of Dr. Clark produced these effects at a level of six percent. The clear implication here is that the mask is psychologically impressive to the human subject and can obscure the determination of the effect of epinephrine and thus the level at which cardiac sensitization becomes a hazard.

I also heard Dr. Reinhardt say yesterday that both 1301 and 1211 are pretty much in the same boat from a hazard standpoint and that, I believe, is a fair summary of the situation.

DISCUSSION

Mr. Wands: I wonder if either of these corporations have a plan for obtaining the necessary human exposure data to evaluate the NFPA standards, or to relax the standards? We can hardly put these out on the basis that there have been no incidents so far, because for one thing we do not have measures of the exposures that these people have encountered in their accidental exposures. I think we have to have a very carefully controlled set of studies. I wonder if either corporation does have solid plans under foot now for experimental toxicology programs?

Mr. Roberts: These tests are very expensive, as you all know. The way to approach this, I believe, is to be first of all sure that the experimental system is one which meets the criteria of the people who are finally going to judge the validity of the results, and that should be done first before we all go through the same kind of difference of opinion which I just alluded to. Then I think there is no reason that this could not be a cooperative effort on the part of all interested parties.

Does that answer your question? Let us put it this way. Certainly we will be among these. Doing it all by ourselves alone, we might think about it, but I don't know the purpose which should be achieved from this. It would be still better, and would be achieved more rationally by a collaborative effort.

Mr. Clark: I should comment just briefly on this that if somebody comes along with more human data, which shows the results were rather severe, we would like to accept that data and we could then modify it. But on the basis of animal experimentation, I would not like to see the application of it reported.

Mr. Kerr: I understand then that the answer to Mr. Wands' question was "no." He asked if there was a specific test plan in the mill, and I didn't hear about it. But certainly the implication is valid that we would not want to go modifying standards without suitable testing.

Just at lunch time I was looking over the German data on halons. I note a set of curves in there which I have not had a chance to look into in any depth which establishes lethal thresholds, and indicates that one should stay below that as distinguished from taking the other approach. That is an interesting bit of comparison that I am not prepared to expand on, because that is all of the reading I have done so far.

Mr. Bischoff: Is there a standard in England for the application of BCF systems?

Mr. Edmonds: In Britain we don't have any standards for systems because we don't have money to set up an organization like the NFPA. What we are doing, and the reason we are here, is that we use NFPA standards in Britain. We might modify them. For example, we don't necessarily have to follow them slavishly. So the answer is no, we have no body like NFPA in Britain, and we work to NFPA standards.

Unidentified: Since this topic of toxicity came up again, I talked with Dr. Rainaldi a little bit yesterday about it. Some of us have read translations from the Italian newspapers about the death of an experimenter and others have heard rumors about this. I wonder if Dr. Rainaldi could take this opportunity to comment on it.

Dr. Rainaldi: I don't know whether I could explain very well in English what I would mean. This gives me an opportunity to clear up some misunderstanding or misapprehension about the facts of that report that came out a couple of years ago.

The first thing is this. According to the information that was received, the magistrate has released a statement and report at the November of that year stating that the Halon 2402 cannot be held responsible for the death of Professor Caranni. However, it can be, but has not been demonstrated, that Halon 2402 could have added some effect to the excitement that Professor Caranni had during the experiment, causing his collapse but not his death. The case is now closed, and this is the official version of what we know about his death, and we don't know any more because we don't have the document in our hands. Maybe the document could be requested from the Milano magistrate.

At the same time, it is very important to recall the facts surrounding this. Professor Caranni was not the man under experiment. He was running the experiment, and was not subject to exposure to Halon 2402. As a matter of fact, just to describe a little bit of what happened, there were two rooms, separated by a wall. In one room there was a man who was a physician who was under experiment. In the other room was Professor Caranni. The man under experiment was submitted to a concentration of 3.5 percent by volume. This was checked by analytical methods and that was quite the right level. After one minute and forty seconds of exposure, the man under experiment went into a heavy anesthesia state. Professor Caranni at that time may have thought that something wrong was occurring to the man under experiment. So, he left his room, went into the other room, and opened the window. Then he came out of the room, and asked for his two assistants who pulled the man out from the room.

When they had gotten the man to the door, Professor Caranni realized the man was still connected to the apparatus by the electrodes, so he went back into the room to unplug the wires and the electrodes. The man was pulled out, but when Professor Caranni came out from the room, he collapsed. The man under experiment recovered very quickly, in a matter of a minute or so, and he himself helped Professor Caranni. My assistant in the lab who did the heavy job of pulling out the man under experiment did not suffer any effects at all. Professor Caranni was still alive when he was brought to the aid room. What happened after that morning, we don't know. What we do know we have stated to the legal authorities.

Mr. Kerr: I hope if you do receive any technical data from the deeper investigation you will share it with us in due time.

Dr. Rainaldi: As I said yesterday, we are conducting an experiment, and we hope in May or June to have the data we expect to have.

IV ENGINEERING SESSION

Chairman, James W. Kerr

REMARKS

Mr. Kerr: I would like to move on now into Session IV with a brief introduction. It was my intention when I put this session together, and as Bill Christian and I talked about what the object of the game should be, to present some answers to a number of practical questions and present them from several points of view, hoping that by the end of the afternoon we would have a better feeling for whether or not we had answered the questions, or merely raised them. There are dozens and dozens of questions that one could go through, and if I were making this introduction at 1:00 o'clock in the afternoon instead of 1:45, I would raise a few of them right now. But they have to do with questions of who should consider installing a system, where there is advice available, discussions of codes pro and con, ideas from availability of material, and actuation mechanisms, hoping that controversial points would be addressed, and a bit of the practicalities from the standpoint of a card-carrying fire chief. Some of this might tell chemists or biomedical specialists more about the end product than they wanted to know, but I believe the concern with the final resting place of the product is an essential element of planning, so we would not apologize for getting into depth on that.

Now, because of airplane schedules and whatnot, we will shuffle the order of the speakers just a bit, but not much. So, the papers will be run through in the order in which you have them in the program. I have a question that is troubling me personally, though. I recently had a letter from a friend in a South American country who asked if I could find him a half a pound of sodium naphthaline acetate. I can't even find that in the book. It is alleged to be an agricultural chemical. So I figured if I told him I asked a meeting at the National Academy for help in finding a half pound of sodium naphthaline acetate and I still could not find it, he would forgive me. If anybody knows where to find it, let me know, will you?

The first paper in Session IV is by Robert Wickham on "Engineering and Economic Aspects of Halon Extinguishing Equipment."

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ENGINEERING AND ECONOMIC ASPECTS OF HALON EXTINGUISHING EQUIPMENT

Robert T. Wickham

Wickham Associates

For the most part, the topics discussed to this point in the program have been oriented to the scientific knowledge that has been amassed concerning the properties and behavior of the halogenated fire extinguishing agents. Since the engineering profession is dedicated to the practical application of scientific knowledge, it is appropriate at this time to relate the capabilities of halogenated extinguishing agent systems to the "real world" situation.

Although there has been significant development activity relative to both Halons 1211 and 1301 in fire extinguishing systems, Halon 1301 has achieved predominance in the United States primarily due to greater efforts by its proponents. The strengths and weaknesses of the two agents are identical with differences only in degree, and within the next few years we can expect Halon 1211 to be developed to a high level of acceptance in the United States. However, for the purposes of this paper, only Halon 1301 total flooding systems are considered since this is the only type of system presently commercially available in the United States.

If one is faced with making decisions about the use of Halon 1301 total flooding systems, he will be much more comfortable if he has some answers to three rather fundamental questions:

1. In what types of applications are Halon 1301 total flooding systems <u>appropriate</u>?

2. What is the <u>cost</u> of a Halon 1301 total flooding system?

3. What are the major engineering considerations in the employment of a Halon 1301 total flooding system?

In order to assess the appropriateness of these systems, we might review some of the characteristics of the agent that were discussed earlier on the program.

1. Halon 1301, stored as a liquified compressed gas and delivered to the hazard in the form of a superheated vapor, has a high extinguishing effectiveness per unit weight, is readily distributed

throughout volumes congested with obstructions, and leaves no agent residue.

2. Although Halon 1301 has toxic properties, it will not present a hazard to life if employed within the guidelines of NFPA Standard 12A*.

3. Halon 1301's extinguishing effectiveness is predictable and reproducible in the 3 to 6% concentration range for most flammable liquids and gases.

4. Halon 1301, in design concentrations of 4 to 6%, is capable of producing complete extinguishment in deep-seated Class A fires; however, it does achieve flame extinguishment and the prevention of flame propagation in these situations.

5. To insure complete extinguishment of deep-seated Class A fires, a Halon 1301 design concentration of 18 to 20% is necessary.

On the basis of these agent characteristics, we can make two rather immediate conclusions. First, a properly designed Halon 1301 total flooding system will produce complete extinguishment in an ordinary Class B hazard, and will provide a life supporting atmosphere and no agent residue after discharge. In applications of this type, Halon 1301 total flooding systems are not only appropriate, but are the only extinguishing systems presently available that have both the life supporting and no agent residue characteristics.

The second immediate conclusion, which is not quite as positive, is that there is a degree of uncertainty about the ability of a Halon 1301 total flooding system, utilizing concentrations in the 4 to 6% range, to completely extinguish fires in Class A materials. This uncertainty is a direct result of our inability to predict, in a practical manner, whether or not a fire in a given Class A material will be surface or deep-seated in nature.

Since the first conclusion is rather clear, simple and widely accepted, we might concentrate on the implications of the "uncertain" conclusion concerning Class A materials.

Life would be simpler if we were able to say that a Halon 1301 total flooding system is capable of extinguishing any type of fire with a five percent concentration. We would then have a nearly perfect general purpose agent, we could write clearly defined rules for its use, and the application engineering associated with the systems could then become "cookbook."

Instead, we are faced with an agent that is "almost" ideal, with its major limitation being the uncertainty of its performance in low,

* "Halogenated Extinguishing Agent Systems - Halon 1301," NFPA Standard 12A - 1971, National Fire Protection Association, Boston, Massachusetts.

4 to 6%, concentrations on Class A materials. Recognizing this, the potential owner of a Halon 1301 system for a hazard containing Class A materials has a number of alternatives:

1. He can elect not to use Halon 1301 and either go unprotected or use another agent and forfeit Halon 1301's combined no-agent residue and life safety features.

2. He can use Halon 1301 in the 18 to 20% concentration range and forfeit its life safety feature.

3. He can use Halon 1301 in the 4 to 6% concentration range and make some additional provisions to ascertain that his fire protection objectives of business continuity, life safety, and minimization of property loss are achieved.

Up until about a year ago, the first alternative was the one most often selected -- that is, to not use Halon 1301 systems on hazards containing Class A materials. However, people are now recognizing that the advantages of Halon 1301 far exceed its Class A disadvantage; and they are looking for ways to maximize the agent's strengths and minimize its weakness. This trend is becoming very obvious in the protection of computer rooms and record storage areas where the concern over water damage from automatic sprinklers, right or wrong, is quite real. As a result of this attitude, it is becoming commonplace to employ Halon 1301 systems in high value areas containing Class A materials. This is invariably accomplished by employing the system along the lines of the third alternative; that is, using the Halon 1301 in the 4 to 6% concentration range and making additional provisions to cope with deep-seated fires, should they occur.

This method is also being recommended by a large preferred risk insurance group when they are satisfied that the "additional provisions" made to accomplish complete extinguishment of deep-seated Class A fires are both appropriate and likely to occur. Although the "additional provisions" will vary from hazard to hazard, some have been found to be common.

1. Utilizing early detection devices to reduce the possibility that a Class A fire will become deep-seated.

2. Connect the detection system with a permanently manned central station that will provide some fire service response.

3. Incorporate accessory equipment such as dampers and door closers into the system to insure that the Halon 1301 concentration is maintained until the fire service is able to reach the scene.

4. Provide training for the personnel responding to an alarm on actions to be taken at the scene including the extinguishment of any smoldering materials before venting the Halon 1301.

In applications of this nature, Halon 1301 will readily extinguish all flaming combustion and will prevent it from recurring as long

as the 4 to 6% concentration of agent is maintained in the volume. If it is a deep-seated fire, smoldering may continue, but there is little likelihood of the fire propagating before the fire service responds. With this approach, we have capitalized the strengths of the agent and covered its weakness by another means.

The ultimate determination on whether or not a Halon 1301 total flooding system, or any other extinguishing system, is appropriate for a given hazard must be based on the potential owner's assessment of how well it can be incorporated into his overall fire protection plan -- not on what it can do regardless of what else is happening in the world.

Once we have determined that the Halon 1301 system has passed the appropriateness test, the next step is to examine the cost of a system.

Basically, there are three individual elements in the total cost of a Halon 1301 system:

1. The extinguishing hardware portion which consists of the agent, the agent storage container, actuating devices and controls, nozzles and installation drawings.

2. The detection hardware portion which includes the detector heads and appropriate controls.

3. The installation portion which includes labor and materials such as pipe, pipe fittings, pipe hangers, conduit, wire, and other items that are usually locally procured.

Figure 1 depicts the cost per cubic foot of volume for the extinguishing hardware necessary to produce a 6% Halon 1301 concentration at 70° F over a range of volumes.

The second cost element of the system is the detection hardware which is shown as cost per square foot of floor area in Figure 2. This relationship is based on one zone of ionization type detection with each head covering 250 square feet.

Installation material and labor costs are much more difficult to quantify due to regional variations in labor rates and other factors not easily identified. However, an analysis of experience indicates that the installation cost of the extinguishing hardware is approximately 33% of the cost of that hardware; and the installation cost of the detection equipment is 45% of the cost of that equipment.

To try this cost presentation, consider a room with a volume of 20,000 cubic feet and a ceiling height of ten feet, producing a floor area of 2,000 square feet. Referring to Figure 1, the extinguishing equipment at this volume should have a cost of $0.29 per cubic foot or $5,800. Figure 2 indicates that the detection equipment at 2,000 square feet should cost $0.66 per square foot, or $1,320. Installation for the extinguishing equipment is 33% of $5,800, or $1,933; and installation of the detection equipment is 45% of $1,320, or $594. Adding

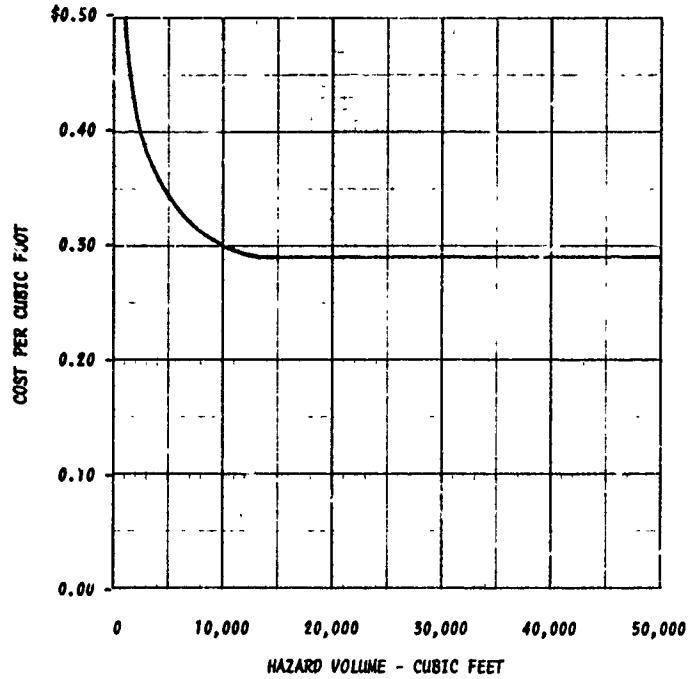

FIGURE 1. Halon 1301 extinguishing system equipment costs (static air, 6% concentration @ 70° F).

these elements produces an installed user cost of $9,647 which is approximately $0.48 per cubic foot or $4.82 per square foot.

As the systems become more exotic than the one described, so also will the costs.

If we have determined that the Halon 1301 system is both appropriate and within our cost limitations, the rest of the task is downhill, since the engineering considerations in a system application are very well defined in engineering manuals published by the equipment manufacturers.

Figure 3 is a flow chart depicting the steps an engineer would most likely follow in order to select the proper equipment and calculate the performance of a Halon 1301 total flooding system. Basically, the design process consists of three distinct phases, the first of which is oriented to the determination of agent requirements. The second phase encompasses equipment selection and location, and the final phase consists of flow calculations to ascertain the discharge performance of the system.

In the application of a Halon 1301 total flooding system, the engineer's initial task is to define the hazard to a point where he has generated the input data for the system design. This hazard definition will include a description of the:

Hazard dimensions and configuration,
Maximum and minimum net volumes,
Fuel involved,
Temperature range in the hazard area,
Ventilation and unclosable openings....
....and the Occupancy status.

After identification of the fuel involved, a minimum design concentration is selected based upon the information in NFPA 12A, actual laboratory experimentation, or manufacturer's recommendations. This concentration, together with the information on the minimum hazard temperature, the maximum net volume, and agent losses due to ventilation or unclosable openings serve as the basis for calculating the minimum agent quantity.

In determining the agent quantity, it is important to remember that it is the volumetric percentage of the Halon 1301 vapor in air that determines whether or not a fire will be extinguished, and it is not just a matter of so many pounds of Halon 1301 per cubic foot of hazard volume. This means that if a certain fuel contained in a room with a volume of 1,000 cubic feet requires a 5% concentration of Halon 1301 to produce extinguishment at 0° F, 23.9 pounds of agent are required, whereas at 100° F only 19.4 pounds are required to produce the 5% concentration.

Once the minimum quantity of agent is selected, a calculation must be performed to determine the maximum possible concentration that

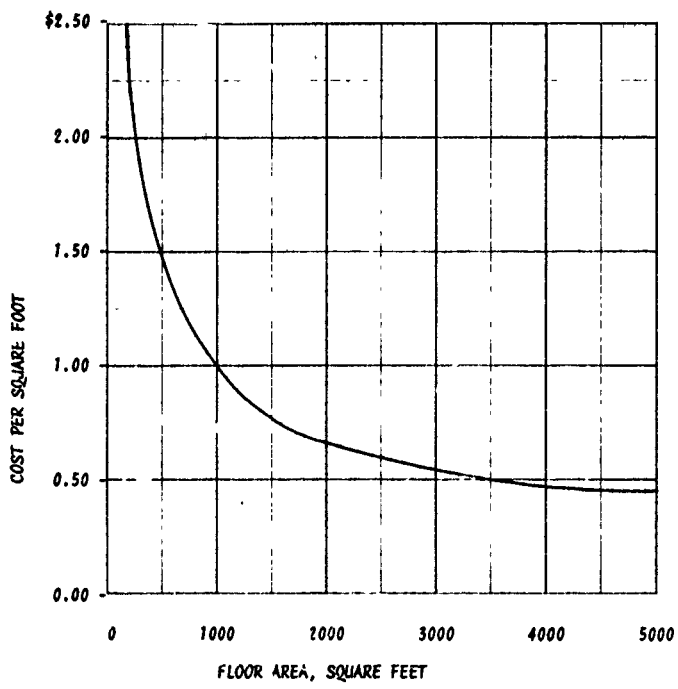

FIGURE 2. Halon 1301 system detection equipment costs. (Ionization heads, one zone, 250 ft^2/head)

would be developed should the system discharge when the hazard is under maximum temperature and minimum net volume conditions. The minimum net volume is that condition when the greatest amount of transient objects are stored in the volume, and is usually applicable only to hazards where the volume fluctuation exceeds 10% of the total volume. If a hazard was protected with a Halon 1301 system designed to produce a 5% concentration at 0° F, and if the system discharged when the ambient temperature was 100° F with 20% of the volume occupied by stored material, the concentration developed would be 7.5%. If there is a possibility of a 50% increase in the concentration, we should at least be aware of it.

Once we have finalized the agent quantity we can proceed with equipment selection and location. The agent tank selection is based upon the minimum agent quantity, and a standard tank is usually selected from the line of one of the equipment manufacturers. These agent tanks, which are specially designed for Halon 1301, are usually DOT

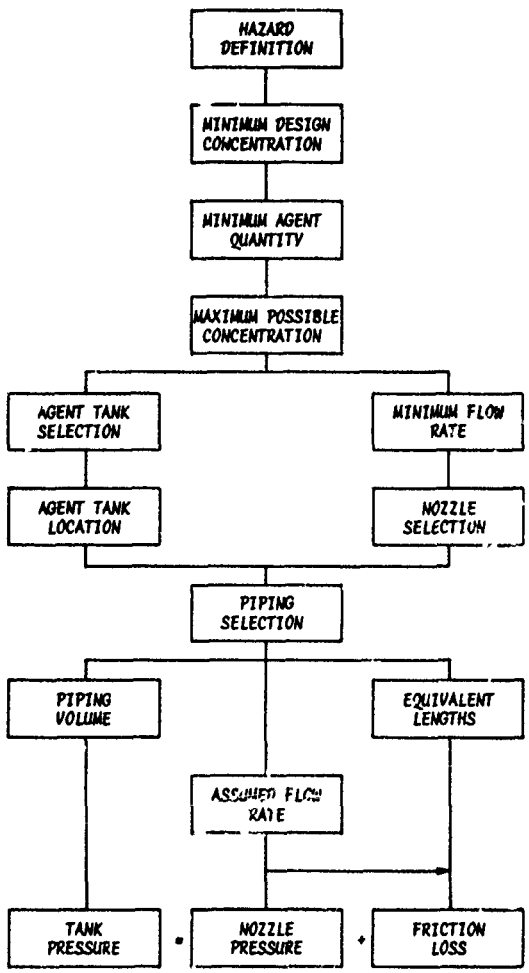

FIGURE 3. Halon 1301 total flooding system design process.

4BA-500 cylinders containing the agent and superpressurized with nitrogen to a total pressure of 360 psig. Next, the agent tank location is determined by selecting a site where the piping to the discharge nozzles will be minimized and at the same time the tank will not be exposed to fire or explosion hazards.

According to NFPA 12A, the system must completely discharge its contents in 10 seconds or less, which essentially establishes the minimum flow rate. This 10 second requirement is intended to minimize the time that less than the complete extinguishing concentration is exposed to the fire, thereby minimizing the amount of halogen acids generated. It is interesting to note that this requirement was based on testing with Class B fuels in which fires develop rather quickly, and that there will be a proposal to the NFPA 12A Committee to reconsider this requirement for Class A fires where the possibility of rapid and complete involvement of the fuel is rather remote.

There are two considerations that must be treated simultaneously in the nozzle selection process. The first is the maximum floor area that the nozzle is capable of covering which essentially dictates the nozzle location or spacing. The second consideration is that the nozzle must be able to deliver its portion of the system's minimum flow rate at a nozzle pressure greater than 199 psig. This minimum nozzle pressure, which is the vapor pressure of Halon 1301 at 70° F, is intended to insure that the agent will remain liquified until it leaves the nozzle.

After the agent tank and nozzle locations are selected, the piping system is then designed to connect the nozzles to the agent tank. The piping selection is based on the agent flow rate and the associated friction loss per foot of pipe. Pipe sizes should be selected to keep this value in the 0.1 to 0.5 psi per foot range. With the equipment now tentatively selected and located, the next phase consists of calculating the agent flow to insure that the minimum rate is achieved. The first step is to express the piping network in terms of equivalent length. At the same time, the internal volume of the entire piping network is determined.

Unlike the flow calculations for carbon dioxide systems where an "average" cylinder pressure is assumed, a somewhat more scientific approach is taken with Halon 1301 systems. A calculation is performed to determine the tank pressure at that instant when liquid Halon 1301 has completely filled the piping network but has not yet left the nozzles. This computed tank pressure is then used in the flow calculations.

An attempt can now be made to "balance" the system by determining the flow rate that will produce a nozzle pressure and a pipe friction loss whose sum is equal to the tank pressure. This is accomplished by using an assumed flow rate, which on the first trial balance should be the minimum flow rate. The nozzle pressure and the pressure drop in the pipe at the assumed rate can be determined from manufacturers' performance information which is outlined in their design manuals.

If in the trial balance we find that the tank pressure is greater than the sum of the nozzle pressure and friction loss, the system will produce a flow rate higher than that assumed and the design is acceptable. If the tank pressure is less than the sum of the other pressures, the system will not produce the required minimum flow rate and changes must be made to the piping, nozzles, or agent tank location to increase the Halon 1301 flow rate. This balancing exercise could become tedious if performed manually, and as a result, most manufacturers of halon extinguishing systems have developed computer programs to handle this trial and error solution.

Since there is a significant difference in the halon system hardware that the various fire equipment manufacturers are marketing, the manufacturer's design manual is really the only document that is specific enough to be used in the design or evaluation of the equipment. For the comfort of those who suspect equipment manufacturers of unobjective behavior, the design manuals have been thoroughly scrutinized by Underwriters' Laboratories and Factory Mutual if the laboratories have listed or approved the equipment.

The appropriateness, cost and engineering considerations of Halon 1301 systems can probably be summarized with these three points:

1. A Halon 1301 extinguishing system is appropriate for a given hazard if the owner is able to intelligently fit it into his overall fire protection plan.

2. Halon 1301 systems are expensive, but so are the things that they protect. Only the owner can assess the cost/benefit ratio for his particular application.

3. Most of the engineering information on Halon 1301 systems has been developed through the efforts and at the expense of the fire equipment and agent manufacturers, and it is to these people the potential owner should turn for factual and complete advice on Halon 1301 systems.

REMARKS

Mr. Kerr: Thank you very much. In the remaining twenty and a couple of minutes before coffee break, by a miraculous act of shoe-horning a longer paper in, George Grabowski will talk about "Fire Detection and Actuation Devices for Halon Extinguishing Systems."

FIRE DETECTION AND ACTUATION DEVICES FOR HALON EXTINGUISHING SYSTEMS

George J. Grabowski

Fenwal, Inc.

In the past, extinguishing systems have depended to a great extent upon the manual release of the agent on the fire. A fire detector or human response would signal the presence of the fire and the extinguishing agent was then manually employed. This has been an adequate approach for protection of the hazards that were being encountered but a change has occurred. Our advanced technology has developed new materials, automated processes, complex computing machines, etc., all of which need rapid extinguishing action due to factors such as increased flame propagation rates or high value density loading. Human response is either too slow for this modern hazard or not available in unmanned areas. All of this is generating a tremendous increase in the number of installations where the system employs one or more detectors to automatically release the extinguishing agent. This has, in turn, prompted the need for a better understanding of the requirements of fire detection and actuation devices for extinguishing systems.

BACKGROUND

Before the sixties, there was little use of automatic systems except for an occasional carbon dioxide or dry chemical system where the hazard dictated this type of system. It was not until the early sixties that there appeared a protection system that had to be automatic under all conditions. This was the explosion suppression system which could not depend upon human response due to the extreme rapid action that was necessary to stop an explosion after it started. The installations that have been made of this system, have proved of immeasurable value since they provided an insight to the requirements of the release portion of an automatic system. Needless to say, some of this experience pointed up the need for a new approach to release devices where consideration is given to such factors as reliability, maintainability, etc., which were hitherto unknown in the fire protection industry. Further, it pointed up the need for a systems approach where all items in the system are thoroughly engineered and understood in accordance with the total requirements. The manufacturers and installers that are now engaged in automatic systems are learning many of these lessons the hard way since they were totally unprepared for taking a systems approach.

In addition to the protection needs dictating an increase in automatic systems, the introduction of halons as acceptable extinguishing agents has also required the installation of automatic systems.

These agents are unique in fire protection in that their extinguishing action is most effective when applied rapidly on the fire in its earliest stages. Failure to handle this material in this manner can result in excessive decomposition. This was recognized by the NFPA Standard 12A Committee who incorporated the following in the Standard:

Para. 1410 - Automatic detection and operation should be used.

DETECTION vs RELEASE

In order to satisfy the need for automatic systems, the industry has turned to the use of available fire detectors, many of which have proven to be totally inadequate for the role of a releasing device. It was found that they had not been designed to meet the more rigid requirements dictated by the function to be performed. A comparison of the primary functions of a fire detector and a releasing device is shown below:

FIRE DETECTOR - To sense the presence of a fire and provide an alarm signal for evacuation of occupants and remote fire call.

RELEASING DEVICE - To sense the presence of a fire and actuate the primary extinguishing system along with providing an alarm signal for evacuation of occupants and remote fire call.

The difference is obvious since the actuating device is providing the intelligence for releasing the extinguishing agent onto the fire. An inadequate device in the single train of protection can render the protection totally ineffective by either failing to sense a fire in sufficient period of time or by inadvertently actuating the system and eliminating the availability of protection until the system is reconditioned. While a false alarm or failure to sense a fire are undesirable in a fire detection system, the consequences of these are more severe for releasing devices from a potential property loss or hazard to life standpoint. A releasing device requires greater performance than a fire detector from a number of standpoints in order to perform the functions for which it is intended.

In order to better illustrate this point, an arbitrary value was assigned to the factors that must be considered in the selection of a suitable system. These were based upon experience that has been encountered to date with both types of unit. These are presented in Table 1 with a rating of 5 being the highest and 1 the lowest.

As can be seen, the ratings for the release of a system are higher than for fire detection alone. These would, of course, vary for a specific application but on an overall basis, the above would hold

true. The conclusion from this is that a fire detector is not necessarily a satisfactory release device while, in turn, a release device will always be a good fire detector.

TABLE 1

Rating of Requirements for Detection and Releasing Systems

	Detection	Release
Sensitivity	4	4
Reliability	3	5
Maintainability	2	4
Stability	4	5

DETECTION OF FIRES

While there are many ways to detect a fire, and much has been written on the subject, proper selection of the technique to be used is still done in a manner that leaves much to be desired. The fire protection industry has always been plagued with the fact that selection is primarily based upon economics and not performance. This basis of selection for automatic systems can be disastrous and the proper approach should be based upon the full understanding of the detector operation and the system performance requirements. This is vital since the design of detection devices for system actuation should be based upon the realization that a fire detector is a sensing instrument and must be applied as such. There is no true fire detector available on the market, that is a detector that will sense only a fire and will not alarm under any other condition. The detectors being used are truly instruments that sense a condition produced by a fire, but may also sense outputs from other sources. One must, therefore, apply the detector with full knowledge of its sensing characteristics and the other conditions present in the environment to which it will respond.

The following is a review of the presently used techniques and the conditions in the installation that could create problems:

FIXED TEMPERATURE - Sensing the temperature in a room and releasing agent at a fixed temperature is one of the most common methods used to date. A temperature rise of this type may, however, be very slow particularly in air conditioned buildings and extensive damage can occur before detection and extinction of the fire.

RATE OF TEMPERATURE RISE - This is one of the most widely used techniques for fire detection since it results in a rapid sensing of the fire condition. Application of this technique must be thoroughly analyzed, since false alarms can occur due to heating systems, machines, etc., and dilution of air from ventilating systems can delay sensing of a fire.

RATE COMPENSATION - This combines the principles of fixed temperature and rate of rise to provide a more reliable unit. Care must still be taken in analyzing the air currents under normal operating conditions to minimize false alarms and insure proper detection of the fire.

PARTICULATE MATTER - A technique of sensing the particulate matter given off by a fire by means of an ionized path. While this type will provide early warning of many types of fires, it is also sensitive to other combustion sources and to pollutants in the air. It is also affected by air currents which divert the particulate matter away from the detector.

VISIBLE SMOKE - A technique of sensing visible smoke given off by the fire by interruption or scatter of light. Care must be taken to insure that foreign matter in the room or device will not cause false alarm. Also affected by air currents that might divert the smoke and delay detection.

FLAME-ULTRAVIOLET - A relatively new technique of sensing the radiation given off by a flame in the 1900 Å to 2500 Å range. It will detect a fire faster than any other technique but will also respond to UV from electric arcs and lightning.

FLAME-INFRARED - This technique has been under investigation for many years due to the high energy level given off by a flame in the IR range. Many other sources also radiate this type of energy and discriminating techniques must be employed.

In addition to consideration of the conditions existing in the installation of a detector system, care must be taken in selecting the proper detector for the type of combustible. The degree of sensitivity to the three classes for fires is summarized in Table 2.

This illustrates the fact that there is no universal fire detection technique which can provide satisfactory detection of all fire. This can also be seen in the test results in Table 3 which summarizes the number of responses of a detector grouping for a series of tests using various combustibles including, heptane, alcohol, and polyvinyl chloride. No single technique recorded a 100% response.

While we have presented the major factors for the selection of the proper detection technique, it is important in the final selection to give careful consideration to all of the requirements of the system. A systems approach to this selection is vital to the successful engineering of the final installation.

TABLE 2

Sinsitivity of Various Fire Detection Techniques

Technique	Class A	Class B	Class C
Fixed Temperature	Low	High	Low
Rate of Rise	Medium	High	Low
Rate Compensation	Medium	High	Low
Particulate Matter	High	High	Medium
Visible Smoke	High	Low	Medium
Ultraviolet	Low	High	High
Infrared	Low	High	Low

EQUIPMENT PERFORMANCE

After selection of the proper detection technique that meets the system requirements, it is necessary to select the equipment with consideration of sensitivity, reliability, maintainability, and stability. The following is a discussion of each of these for the available devices that are on the market.

SENSITIVITY - The sensitivity of the detection device is generally established by the physical design, except in the case of products of combustion units that can be adjusted. All of the thermal devices have fixed spacing ratings based upon the approval testing and the easiest way to increase sensitivity is by reducing the spacing. This greatly reduces the response time to a fire and assures the application of the agent before extensive damage is done. Reduction in spacing is also recommended for the products of combustion units since reliance on the sensitivity adjustment alone can result in a false alarm problem. Sensitivity of the flame detectors is inherently high so this is not a major factor in equipment selection.

RELIABILITY - This factor is not normally considered for fire protection equipment and a requirement cannot be found in any standard, code, specification or approval requirement. It is, however, important that it be considered in automatic systems and worthwhile for discussion in this presentation.

Reliability relates to the ability of the system and each individual component to be in proper working condition at all times ready to perform its intended function. It has generally been

TABLE 3

Summary of Detector Response

Detector	No. of Tests	No. of Responses	% Responses
Fixed Temperature	105	83	79.0
Rate of Rise	52	49	94.2
Rate Compensated	26	24	92.3
Ionization	165	157	95.1
Visible Smoke	122	60	49.2
Ultraviolet	54	52	96.3
Infrared	54	36	66.7

misunderstood when occasionally referred to in fire detection as relating to the ability to repeatedly sense a fire. This actually is the stability of the unit rather than reliability. The aerospace industry has developed reliability to a point where it is incorporated in their system equipment specifications and their methods of analysis should be employed in the selection of the detection units. This generally has not been accomplished and it is only possible to present a general comment of the reliability of available detection units.

The units with the highest reliability are the fixed temperature eutectic units and rate compensated units. The simplicity of the eutectic device gives it high reliability while the sealed construction of the other provides protection that allows the detector to withstand long service life under extensive conditions. The rate of rise units have a slightly lower reliability due to the more delicate nature of the sensing surface and possible failure of the rate function. All of the products of combustion and flame detectors employ electronic components which have a higher failure rate than mechanical devices and result in a much lower reliability.

MAINTAINABILITY - The maintainability of detection units varies directly as the complexity of the design. The thermal units have no periodic maintenance requirements and the degree of maintainability with these units is extremely high. The products of combustion and flame detectors require periodic inspection and servicing to assure that the sensing element is in proper working order. This is not, however, an extensive effort and, therefore, does not detract from these devices.

STABILITY - The stability of a detector relates to its ability to sense fires over extended periods of time with no change of sensitivity. This follows the general pattern of the other factors where the mechanical devices are better than the more complex electronic ones. In almost all the thermal units, there are no materials that have degradation of physical properties with age or usage while this is a known fact with electronic components. Periodic checking of all units with electronic components is necessary in view of this reduced stability.

The above analysis of existing detection devices is very general and the actual performance will vary depending upon the design, manufacture and quality control employed by the manufacturer. In all automatic systems, it is important that only those devices meeting the system requirements be used. A summary of the detector performance is presented in Table 4.

TABLE 4

Detection Equipment Performance Summary

Detector	Sensitivity	Reliability	Maintainability	Stability
Fixed Temperature	Low	High	High	High
Rate of Rise	Medium	Medium	High	High
Rate Compensated	Medium	High	High	High
POC-Ionization	High	Medium	Medium	Medium
POC-Visible Smoke	Medium	Medium	Medium	Medium
Flame - UV	High	Medium	Medium	Medium
Flame - IR	Medium	Medium	Medium	Low

SYSTEM PERFORMANCE

While automatic systems will always require maximum performance, the use of halon as the agent places an even greater emphasis on the important factors in the system design. The properties of halon extinguishing agents that make them excellent combustion inhibiting material necessitates a system design that is different than systems using agents such as carbon dioxide and dry chemical. All of the halons go through some degree of decomposition in order to accomplish their inhibiting action and while the quantity required to extinguish is generally quite small, the cost of the agent is such that it represents a large portion

of the total system cost. Major characteristics of a halon system in the order of importance are as follows:

1. Rapid discharge to minimize the development of decomposition products.

2. Reliable actuation and distribution of the agent to assure positive extinguishment.

3. Early detection and agent release to minimize fire loss.

With these characteristics established as necessary for optimum system design, it is possible to analyze each of the individual components to determine the performance necessary to assure the satisfactory operation. The following is a discussion on each of the components of a halon system emphasizing the factors to be taken into consideration to assure proper selection:

DETECTORS - Since early detection of the fire is not as important as positive actuation, the detection units for a halon system should be considered based upon the reliability characteristics first, and secondly the sensitivity characteristics. Tests have shown that while early detection of the fire is desirable from a loss prevention standpoint, the efficiency of the agent does not require its being discharged on a fire during the incipient stages. The effectiveness has proven to be more closely related to rate of discharge, and many fires have been effectively extinguished after long preburn periods. Therefore, one can sacrifice sensitivity for reliability in order to assure that the system operates when the fire exists rather than at a time when a significant loss has occurred, or not at all.

For this reason, a highly reliable detector should be selected which means, based upon previous analysis of detection units, that a fixed temperature or rate compensated thermal unit should be used for releasing the agent. These units also serve to reduce the possible occurrence of false actuation since they have a high degree of stability. In order to make up for the loss of sensitivity, many systems are being installed with products of combustion detectors for pre-alarm with rate compensated units releasing the agent.

There are variations to this approach where product of combustion detectors and flame detectors are used for system release but both of these should be used under carefully controlled conditions in view of the decrease in certain performance characteristics. There are, however, many cases where the detection sensitivity requirement far outweighs the loss in other performance factors and this should be judged by the system designer after reviewing all of the installation conditions.

WIRING - Since the majority of the units being used for detection provide an electrical signal or contact operation upon sensing a

fire, the selection of the wiring installation becomes very important. Unless the installation is accomplished in the proper manner, the reliability of the detection part of the system can be reduced to an intolerable level regardless of the type of detector being used. The system designer must give serious consideration to this part of the system which has shown to be extremely important in all automatic systems employing electrical signals for release purposes. Realization of this has prompted many designers to specify mineral insulated cable which does provide a high degree of reliability in view of its high resistance to environmental conditions.

Regardless of the type of wiring used in the system, it is important that supervision of all circuits be used in order to provide a trouble signal when a failure occurs. This practice has proven to be of immeasurable value in explosion suppression systems and all halon systems with wiring should follow the same approach.

Redundant circuits are also another technique for improving wiring reliability. This, however, has not been found necessary with halon systems and the above practice of supervision has proven adequate. Only in extreme circumstances would redundancy be necessary in a fire suppression system.

POWER SUPPLY - The power supply, or control unit, in an automatic system not only furnishes the operating power for the detectors but also provides the firing current for the actuation system. The reliability of these devices should also be very high and care should be taken in the use of existing fire alarm panels. Many of these have not been designed to the degree of reliability necessary for automatic systems for the same reason as the fire detector units.

Emergency standby power should also be available for any halon extinguishing system. This can be provided either through an existing emergency circuit or be incorporated in the power supply by means of batteries. The availability of this type of power supply will assure performance regardless of the conditions that have been created by the fire since the system operation is totally independent of the standard available power in the building. Failure to provide this would greatly reduce the reliability of the system and the cost of the protection would be a poor investment.

RELIABILITY ANALYSIS - After selection of the various components in the system, it is possible to calculate the reliability to assure that the required figure has been achieved. For example, if a simple halon extinguishing system was designed using a fixed temperature detector releasing a solenoid valve in a series circuit, the calculation for the mean time between failure (MTBF) would be as follows:

Item	Failure Rate per 10^6 Hours
Thermal Detector	3.0
Wiring	0.6
Solenoid	5.0
Power Supply	1.4
Total	10.0

With a failure rate of 10.0 for 1 million hours, the MTBF, which is the reciprocal, would be 100,000 hours. If a standard distribution is expected, this would mean that 36% of the systems designed in this manner would survive after 100,000 hours, while all others would fail below.

With this MTBF established, the designer can then determine whether the system will perform satisfactorily for its intended function. If the MTBF is too low, it may be necessary to investigate other types of components that would provide a lower failure rate, or derate the usage of the existing units to increase their performance. If it is not possible to change the MTBF in either of these manners, it may be necessary to incorporate a preventive maintenance program, including the replacement of critical items that would reduce the overall system failure rate. All of this involves a thorough understanding of system reliability and the components that are being incorporated into the system.

SUMMARY

The usage of halons in extinguishing systems necessitates the system designer going far beyond the design requirements for systems with other agents. These materials have demonstrated a tremendous capability to improve fire protection for our modern world but the success in achieving this improved protection is dependent upon the fire protection industry taking a true systems approach in the design. Factors not previously considered in this industry must now be understood and accepted as firm requirements to assure performance in accordance with the intended function. The system designer must be responsible for the total system performance and must have complete knowledge of the detection and release requirements in addition to the extinguishing agent capability. The users of these systems must, in turn, be ready to accept the additional complexity in the interest of better protection and not revert to the old practice of protection from purely an economic or insurance standpoint. Halon extinguishing systems hold a great promise in filling a significant gap in fire protection but only a rigid discipline in the industry to assure proper system design will permit this potential to be realized.

REMARKS

Mr. Kerr: In connection with the papers remaining after the coffee break, it is a matter of policy of the Committee on Fire Research that we don't have a symposium without some sort of a white paper, or a document to be issued, either part of or over and above the proceedings volume, a paper which answers the question, "So what? What was the object of the game and where do we think we have gotten, other than talking to each other? What is the state of the art in the particular area that has been addressed?" It is our belief that Rolf Jensen's paper, which will go on at exactly three o'clock whether caffein addicts are in the room or not, because he is going to go on an airplane a few minutes after that, will go a long way toward summing things up along those lines, and will perhaps put a few things into perspective.

If you like, we can entertain a few questions now.

DISCUSSION

Mr. Transue: I would just like to address myself to one item Mr. Grabowski mentioned, that is, the use of the cross-zoning technique with products of combustion detection systems to prevent their premature alarm or false alarm. Cross-zoning with products of combustion detectors is very frequently used to prevent the premature or unwanted release of the extinguishing agent. I don't know of any system where cross-zoning is used to prevent an alarm.

In support of that, for those of you who may not know what cross-zoning is, I would like to define it. Cross-zoning is a system of fire detection where two circuits of detectors, rather than one, are used in the protected space. In that way the agent is not released until both circuits of detectors have detected the fire. This confirms that the fire is first of all a true fire, second that it is a growing fire and should be extinguished.

Unidentified: We had a question on fire protection under the floor of a computer room. We are kind of fighting ourselves on both sides, because now we are opening up the floor because we need more ventilation for the machines. Would it be probable or likely that if we had a high rate of discharge under the floor to get the Class A materials like the cables and things like this, with that high rate we could get the Class A fire, and by all the openings eventually accomplish a volumetric extinguishment, and not hazard any people who might be in the room. We could accomplish something we have said now we can't do.

Mr. Wickham: Maybe I could restate your question. I am not certain I understand it. Tell me if I am wrong. Your question is if in a subfloor area in a computer facility you apply the agent at a high mass rate, would that particular rate be of such an intensity that it would overcome the Class A shortcomings that we have identified with Halon.

The answer is, or my answer is, I am not certain it would or it would not, but if you get into situations like this, you are on the hairy edge of going from a total flooding system to local application system where per cent concentrations really don't mean as much as they do in total flooding, and the direct application of the agent onto the hazardous surface will certainly make a difference. In this particular industry, the way we resolve these things is usually by testing them.

Dr Call: About an hour ago we got a question from Mr. Wands which intrigued me, and I was not at all satisfied with the answer. It had to do with human exposure to the Halons. Yesterday we heard the description of a facility at the University of Wisconsin that is available for this kind of work. We heard a statement that work has to be cooperative. It does not seem to me that it is too expensive to do more human exposure to these kinds of problems, and also if more human exposure was done, it seems that the same amount of money spent for that would do far more about making the compounds salable to the public than normal public relations work.

Mr. Roberts: I think your question is very fair. However, I think the emphasis on the answer as to colaboration which Mr. Wands' question -- I have not had too many meetings to check this out -- covered, this was not focusing so much on cost as on the fact that in order to be valid and useful, I think these tests should involve various people who have an interest and a role. Does that answer your question?

Mr. Kerr: In other words, multidisciplinary aspects do get expensive, and I know that is true for sure.

REMARKS

Mr. Kerr: There are two papers remaining this afternoon, the summing-up paper, which will be on in a very few minutes, and this "practicalities" paper. As we were putting this session together in consultation with Chief Vickery of Seattle, we got to thinking about what the practical considerations were from the standpoint of the man in your community who has to live with fire on a day-to-day basis, the protection, prevention, and all of the other aspects. So Gordon Vickery, who is also a member of the Committee on Fire Research, by the way, and I collaborated on a bit of presentation here. I believe his credentials are impeccable as the Chief of Seattle. I guess the only blemish on his record is that he is not here today to defend himself. As to myself, I am a volunteer firefighter in Fairfax County. Even more than

that I suffered from halogenated hydrocarbons back in the twenties when I was growing up in the Far East, and along with all of the native kids, we foreign kids got worms every year, and every spring we had to be wormed, as people do for their dogs nowadays around here. But back then the state of medicine was such that the standard treatment every spring for all of us under the age of, I believe 14 or 15, was a tablespoon full of carbon tetrachloride -- really two tablespoons. You drank it out of a glass, two doses 12 hours apart, four doses of epsom salts, and nothing but jello to eat for 36 hours. If you think I don't hate halogenated hydrocarbons, you are wrong.

PRACTICALITIES OF HALONS FROM THE FIREFIGHTER'S VIEWPOINT

James W. Kerr, Office of Civil Defense

and

Gordon F. Vickery, Seattle Fire Department

Halogenated hydrocarbon compounds have affected fire department plans and operations for many years -- ever since the mixed blessing of carbon tetrachloride came on the scene. We can remember veterans' housing after World War II where each apartment received one or more 1-1/2 quart Army surplus chemical decontaminating squirters, all filled with carbon tet and accompanied by conflicting instructions. The systems have come a long way since then, but arguments continue, as you have heard in these last two days, and fire departments are under increasing pressure to coexist with various chemical and hardware arrays.

Certainly, halons are permitted where suitable, are even encouraged in some cases. Their manufacture, transport, distribution, installation, and use add a training burden on fire departments, but existing codes and regulations are generally adequate.

APPLICATIONS

The simple matter of cost makes halons useable in only high-value or special hazard (sometimes temporary) facilities. For example, it has a close-to-perfect record in protecting Boeing airplanes under construction. Use in computers or computer rooms, vaults (fur or bank), and various electronic installations has proven its merit. But the cost of 50 cents per cubic foot protected, when compared to 10 to 15 cents for CO_2, or 5 cents for sprinklers, restricts its applications. Thus, firefighters have to look for halons in areas where low weight-to-volume ratio, cleanness, and relatively breathable atmosphere can overcome the cost penalty.

The qualities that make halon a good agent for equipment and limited area protection do not, however, automatically make it a suitable universal substitute for sprinkler protection. That is, one should insist on high-temperature head sprinkler protection for the structure of a room housing computers, even though the computer itself had halon protection. There is a possibility that halon systems could be designed to receive a back-up charge (refill) of additional halon, or even CO_2, delivered by the fire department when the original system was triggered by a fire. Details of this and the manner of funding fire department supply and equipment remain to be worked out, but the concept is valid.

FIREFIGHTING IMPLICATIONS

Halon systems impose several requirements on fire departments, right from the outset:

Installation requires prior engineering approval by the fire department.

All command personnel who might respond to a halon-equipped facility will have to have knowledge of the system, its limitations, and how to activate or inert it.

Pre-fire plans will have to include the halon system. Central planning, such as might involve civil defense, could be useful.

There is a significant potential toxic hazard from a halon system that has discharged but has not controlled the fire. Self-contained breathing units will have to be used, if there is any doubt, as a minimum.

We are concerned with explosive rupture of halon containers exposed to a fire. Dual approved relief devices tested by certified contractors or boiler inspectors are needed.

TRANSPORTATION

Existing regulations on the transportation of compressed gases in ASME or DOT approved containers apply to halon and when properly implemented are sufficient to control halon cargoes. Separate transportation of explosive actuating devices is necessary for safety. General preplanning for potentially hazardous cargoes should suffice for most municipal departments. Identification of cargoes during a fire can be a problem at any time and any place. The International Association of Fire Chiefs is now engaged in making representation to the National Commission for Fire Prevention and Control on this very subject.

INSTALLATION

The installation of a system must conform to N.F.P.A. Standard 12A, and is subject to fire department review. In addition to the safety and relief devices noted above, we would be concerned with any installation that would expose untrained personnel and/or the public to a halon discharge. (Boeing has had some experience with accidental discharge of portable halon units which indicates that shock effects are not severe, but the gas itself can pose a serious hazard.)

The detection and alarm portions of any halon system should be interconnected with the building fire alarm system. Central fire station connection is to be encorraged. All systems should have a readily distinguishable indicator, showing whether they are full or discharged.

Fire department actuation of a large halon system costing several thousand dollars to reload poses a new problem. It is axiomatic that a

fire department can and will use proprietary fire protection equipment when necessary. However, in view of the cost of recharging large systems, it might be proper to have a prior written agreement, preferably executed at the time of installation.

Obviously, each halon system will have to be engineered for the job. Already fire departments have had to discourage individuals from installing groups of small cylinders with individual actuation in large areas. The obvious problem here is incremental discharge of gas, in insufficient quantity to control the fire, with the resultant generation of toxic products. Such generation does not usually occur in dangerous quantities if the halon controls the fire.

THE FUTURE

It is interesting to speculate on the future applications of halon. An increasing use in hospitals and institutions is foreseen, and it could be the answer for protection of high-rise buildings. The cost (and unfortunately the architectural appearance) of sprinkler systems has prevented their universal installation. A one-floor charge of halon could be stored in a high-rise building for automatic discharge. A fire department truck could supply a second shot for the fire floor, plus inerting of the floor above. Such a system is conceivable, and could be less expensive than sprinklers in existing buildings, though a water standpipe back-up would still be necessary.

Codes must be kept up-to-date, and their enforcement improved. Use of halons under proper controls is to be encouraged, but both planning and operational factors must be reflected in fire department training.

REMARKS

Mr. Kerr: Just in case there are any doubts about the credentials of our summarizing speaker, Rolf Jensen, he is not only head of fire prevention at IIT, but also head of you-know-what NFPA committee.

SUMMARY

Rolf Jensen

SUMMARY

SYMPOSIUM ON AN APPRAISAL OF HALOGENATED FIRE EXTINGUISHING AGENTS

Rolf Jensen

Illinois Institute of Technology

Of necessity this summary must be divided into two distinct parts. The first deals with the toxicological studies, papers, problems, and results associated with the halons and with combustion products generally. The second is concerned with the value of the halons as extinguishing agents. Since the data contained in these summary statements is drawn exclusively from the formal papers which have been presented in this symposium and from the associated comments made from the floor and from the podium during open discussion sessions, no attempt is made to provide references or a bibliography.

TOXICOLOGY

Verified field history on toxic exposures to the halons is scarce -- especially in regard to precise pathological examination and exposure history of apparent halon related fire exposures. There are few documented exposure cases with or without injury.

The toxicological effects of the base agents seem to be well defined and supported by research. The physiological consequences of exposure at different concentration levels based on animal and human testing are established. They do not seem to be cumulative. There is a recognized cardiac problem potential; a cardiac problem may also develop on exposure to some hydrocarbons, a less recognized fact. For the most part the levels of toxicity occur above the level where flame extinguishment is achieved.

There is minimal information on synergistic effects in regard to both halon-hydrocarbon and halon-combustion products combinations.

The incremental affect of CO and other combustion products on post-fire survival is only beginning to be studied, but indications are that CO and acrolein are of major concern.

There is some question whether or not the incremental contribution of the halons to the basic exposure inherent in a real fire situation is sufficient to be of concern. The lack of toxicity studies in real fire exposures make it difficult to place other toxicity data in clear perspective in regard to this incremental effect.

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Risk-benefit analysis often predicts the agent usage conditions. Faced with a choice of certain death by fire versus a hope to live, the user may have to take a greater exposure risk as, for example, in a submarine or hyperbaric chamber.

Available test data shows that faster extinguishing and discharge times produce lower amounts of toxic and corrosive halon decomposition products and lower CO.

There is much duplication of research effort and some lack of relationship to real conditions. This indicates a need for stronger cross ties between medical-pathological research efforts, and for feedback information and cross-ties with the FPE practitioner. In this seminar, it was evident that few medical people attended the second day to hear the practical side of the problem. It also indicates a need for a NFPA or other committees to study the broad questions of extinguishing agent toxicology and post fire effects (including both toxicology and other medical effects). Such a study could yield a broad benefit in reducing fire-caused death and injury by developing improved first-aid measures and by providing confirmed base information which may be useful to groups writing performance standards.

Available data supports the recommendations of NFPA Standards 12A and 12B in regard to tolerable human exposure concentrations with an adequate safety factor.

EXTINGUISHMENT

While it is clear that the halons are effective fire extinguishing agents, the degree of effectiveness depends greatly on the goals to be attained. The effectiveness measure may be totally different depending on whether you are trying to protect a computer or an airplane. Effectiveness may be defined in terms of control, extinguishment, rate, quantity, time or cost with varying results depending on whether the agent or the system is tested.

There is available data to support existing recommendations of NFPA 12A and 12B for extinguishment of surface fires by total flooding. Much data is needed to enable development of local application approaches -- and to enable system cost to be reduced as a long range goal.

Data on deep-seated and other Class A fires is less prevalent and it is apparent that more information is needed. Hazard associated with configuration is an apparent factor which has not been quantified, not only in relation to halons but in relation to extinguishing Class A fires in general.

When fires are extinguished rapidly and completely, the level of halon decomposition products produced is so low as to be of no concern in regards to both toxicity and corrosivity. Agent contact time with flame and hot surfaces appears to be the critical factor.

To maximize the benefits and minimize the failings of halons, it is highly desirable to detect, actuate and discharge in the shortest

possible time. This demands a new level of sophistication in fire protection technology and a systems approach. It requires that the total system be evaluated and that detectors and actuators be selected based on hazard and the environment. Automatic detection and actuation is usually a necessity. Speed of detection should be in balance with needed response, the type of hazard, and cost or nuisance of false trips.

Fire department and fire brigade personnel must be trained in the use of halons and systems and understand that a fire, missed by a halon, must be fought while using self-contained breathing equipment. Where flame extinguishment and fire control is the basis of design, they must be promptly notified and trained in the proper "mop-up" action to take.

The halons appear to have good application in many specialized situations -- particularly where value density is high and where risk-benefit analysis supports its use. Examples are aircraft, mines, spacecraft, tanks and computers.

Considering the relation between recognized toxicity levels which produce measurable unwanted effects on humans and concentrations needed to obtain extinguishment, the halons have many useful and valuable safe applications. The halons positively overcome the disadvantages of extinguishing concentrations which do not support life -- previously the only solution where clean agent flooding extinguishment was indicated. They are especially useful where rapid fire control is mandatory.

If the total capabilities of the halons are to be exploited for the benefit of the public, better toxicity data must be developed, especially in regard to Halons 1211 and 2402, and in regard to incremental toxicity effects introduced by halons over and above the toxicity of usual combustion products. Also, better data is needed on fire extinguishment by halons through local application and in Class A fire situations. The responsibility for this research belongs to the proponents of its use.

REMARKS

Mr. Kerr: We thank you for that summation. Unless there is anything else anyone wishes to bring before the assembly, please accept the thanks of both committees to all of the authors and/or speakers in case they are not the same, and especially our thanks to the audience for their patient sitting.

ADDITIONAL PAPERS

(Not Presented at Symposium)

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TOXICOLOGY OF HALOGENATED AGENTS (HALON 2402)

Ralph C. Wands

National Research Council

This paper will review very briefly the literature on the inhalation toxicology of Halon 2402, 1, 2-dibromotetrafluoroethane, and of its pyrolysis products. It is of interest for fire extinguishing purposes because it is a liquid having a boiling point of about 47°C and a density of about 2.16 grams per milliliter. These properties permit the compound to be delivered to the fire as a stream where it can then evaporate rapidly. Its vapors interfere with the chemical reactions of combustion.

An early screening evaluation of the acute inhalation toxicity of halogenated agents was conducted by C. C. Comstock and his co-workers at the U.S. Army Chemical Center in 1950 (1). They exposed rats, one at a time, to a series of increasing concentrations for 15 minutes each. The lowest concentration causing death was reported as the Approximate Lethal Concentration (ALC). For Halon 2402 the ALC was 1336 mg/L, which is equivalent to 12.5% by volume. The comparable values for Halon 1301 and Halon 1211 were 5075 mg/L or 83% and 2203 mg/L or 32% respectively.

Comstock also exposed rats similarly to the pyrolysis products of the agents as produced by passing the vapors through an iron pipe heated to 800°C. The ALC for Halon 2402 decomposition products was 0.16% or 17 mg of starting compound per liter. For 1301 it was 86 mg/L or 1.4% and for 1211 it was 52 mg/L or 7.6%.

MacNamee has reported the pathology studies on these animals (1). The rats exposed to Halon 2402 showed pulmonary irritation with a heavy infiltration of polymorphonuclear leucocytes throughout the lungs and serosanguinous material in many of the alveoli. The decomposition products of Halon 2402 caused pulmonary edema which occluded the lumen of the trachea and most of the alveoli. Similar effects were observed for Halon 1211 or its pyrolysis products.

In 1960 Engibous and Torkelson at Dow Chemical Company, under a contract with the U.S. Air Force Aeromedical Research Laboratories, Wright-Patterson Air Force Base, investigated many of these compounds more thoroughly (2). They found that the effects of short exposures at high concentrations of Halon 2402 primarily involved the central nervous system and death resulted from anesthesia. Fifteen minutes at 26-28% or 2800 to 3000 mg/L did not kill any of the 8 rats; however, a 30-minute exposure was fatal to 2 out of 4 rats. Six minutes exposure at 1280 mg/L, approximately 12% by volume, killed all 8 rats and 1 out of

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8 guinea pigs. Half of this concentration, i.e., 640 mg/L or about 6%, killed none of the 8 rats and 8 guinea pigs exposed for one hour. A 7-hour exposure at 107 mg/L (1%) likewise killed none of the animals. Survivors were sacrificed and autopsied at 18 to 21 days after exposure. Slight injury was found to their livers and kidneys.

They pyrolized the halons at 610°C and found that the toxicity of the pyrolysis products increased in the following order: 1301, 1211, 2402.

Rainaldi in 1968 summarized preliminary data from an Italian laboratory as indicating that Halon 2402 was "a relatively harmless substance" whose pyrolysis products caused "no mortality in laboratory animals during 4 hours of exposure or the subsequent 14 days." Upon autopsy there were "no pathological elements or phenomena" (3). The data behind these statements have not yet appeared in the literature so it is not possible at this time to compare the procedures and results with those reported above. The pyrolysis products evolved from fire extinguishment in a metal box.

Rainaldi also reported, "The amount of Halon 2402 used to extinguish fire is 100 times lower than the Approximate Lethal Concentration (ALC). The quantities of hydrogen bromide and hydrogen fluoride present in the smoke are, respectively, 56 parts per million and 5 parts per million -- considerably lower than their ALC."

The 1965 report in the Russian literature by B. C. Karpov has been translated by the Joint Publications and Research Service of the U.S. Department of Commerce (4). He found that for mice two hours at 430 mg/L or 4% was the "Absolute Fatal" exposure. The "Average Fatal" exposure was 2 hours at 300 mg/L, 2.8%, and the "Minimum Fatal" was 190 mg/L, 1.8%. The "Maximum Tolerated" exposure was 150 mg/L, 1.4%, for 2 hours. He also reported that 14 mg/L, equivalent to 0.13%, was the average concentration which interfered with an unconditioned reflex response in rabbits. Using these data, Karpov has recommended that the Maximum Permissible Concentration of Halon 2402 in the air of production buildings should be 2.0 mg/L. That is less than 0.02%, presumably for an 8 hour exposure daily.

In the last two or three years a group at the Albany Medical College of Union University have been studying the effects of halogenated hydrocarbons on the mitochondria of animals exposed by inhalation. Their work has been done under a contract with the National Aeronautics and Space Administration (5). The preliminary data show that the mitochondria of lungs and brains of rats and mice are more affected than those of hearts, kidneys, and liver following exposure to Halon 2402. Significant changes in enzymic activities of these mitochondria result from exposures of the animals for 10 minutes at 460 mg/L, that's 4.3%. Changes also result from repeated exposures daily for one hour for up to 6 weeks at 310 mg/L, 2.9%, for rats and 138 mg/L, 1.3%, for mice.

None of the Halon 2402 toxicology studies reviewed above have reported upon what appears to be one of the most critical toxic effects of the halogenated hydrocarbons, namely, cardiac sensitization to

epinephrine. A private communication received recently at the Advisory Center on Toxicology (6) indicates that concentrations of about 27 mg/L of Halon 2402 produces marked cardiac arrhythmias in all exposed dogs with several deaths from ventricular fibrillation, that is only 1/4 of 1% by volume in the air. The details of exposure conditions such as time or epinephrine concentrations are not available. This report certainly needs to be investigated more thoroughly.

REFERENCES:

1. Army Chemical Corps, "An Investigation of the Toxicity of Proposed Fire Extinguishing Fluids," Army Chemical Corps, Army Chemical Center, Md., MDRR 23, 1950.

2. D. L. Engibous and T. R. Torkelson, "A Study of Vaporizable Extinguishants," Wright Air Development Division, WADC-TR-59-463, AD 239 021, January, 1960.

3. N. Rainaldi, "Halon 2402," Fire J. 63:37-38, November, 1969.

4. B. C. Karpov, "Investigations in Industrial Hygiene and Occupational Pathology: Material on Toxicology of Chronic Effect of Freon-22, and Lethal and Threshold Concentrations of Freons," Translation from: Issled. Gig. Truda i Profess. Patol. 75:231-240, 241-249 (JPRS 28, 721; TT:65-30312) 1963.

5. E. Bachmann and L. Goldberg, "Effects of Halocarbon Compounds on Rat and Mouse Mitochondria Following Exposure in Vitro and in Vivo," Toxicol. Appl. Pharmacol. 19:391-392, Abstract No. 77, 1971.

6. Private Communication: Advisory Center on Toxicology, National Academy of Sciences, Washington, D.C., 1972.

DEPENDENCE OF EXTINCTION TIME AND DECOMPOSITION OF HALOGENATED EXTINGUISHING AGENT ON ITS APPLICATION RATE

Shuzo Yamashika

Fire Research Institute, Japan

SUMMARY

Since the extinction time and the decomposition of a fire extinguishing agent are both dependent on its application rate, the latter is considered as quite an important factor in fire extinguishment. In this report, the results of a series of fire extinguishing tests with halogenated agents were analyzed by the aid of a formula expressing the relationship between the application rate and the extinction time. On the basis of this formula, the critical application rate for halogenated agent is discussed. Further, the experimental values of critical concentrations for this class of agents with enclosed fires and those of critical quantities of agents per unit volume of fuel evaporated with tray fires in the open are compared with the calculated values based on the data given in various literature sources.

NOMENCLATURE

$c(ML^{-3})$:	Concentration of agent.
$c_r(ML^{-3})$:	Critical concentration of agent.
$Q(L^3T^{-1})$:	Rate of ventilation with the enclosed fire or rate of flow of combustible gas-mixture into flame with the open fire.
$q(MT^{-1})$:	Application rate.
$q_c(MT^{-1})$:	Critical application rate.
r :	Fraction of fuel in the mixture of fuel and air at c_r.
$t(T)$:	Time.
$t_e(T)$:	Extinction time.
$t_c(T)$:	Time required for the concentration of agent to reach c_r.

$t_a(T)$: Additional time (usually about 0-5 seconds) defined as $t_a = t_e - t_c$.

$U_A(L^3T^{-1})$: Air supply rate.

$U_F(L^3T^{-1})$: Fuel supply rate.

$V(L^3)$: Volume of the space for enclosed fire or flame itself for open burning.

INTRODUCTION

It is well known that, with any fire extinguishing agent, the extinction time will be increased as the application rate is decreased, and vice versa. When the application rate is decreased below a certain critical value, the fire cannot be extinguished. Of various formulae heretofore presented to express the relationship between the application rate and the extinction time with enclosed fires, the author favors a formula of exponential type. It is also suggested that the same equation can well be applied to the extinction of tray fires in the open instead of a formula of hyperbolic form. Further, the decomposition of halogenated extinguishing agents was examined to show that it is directly proportional to the extinction time. This is explained by presuming that the decomposition takes place exclusively within the flame. Thus, the toxic gaseous products decrease as the application rate is increased and the extinction time is decreased, within a range that may be economically feasible.

EXPERIMENTAL PROCEDURES

The extinguishing tests were made with enclosed fires and with fires in the open, as well.

The space volumes for enclosed fires were threefold, i.e., 0.64 m^3, 2.1 m^3 and 29 m^3, and the tests were made with a variety of fuels such as hexane, wood crib, charcoal, paper, rubber, and some plastics. In each test, an adequate preburn time was provided before the application of agent.

The open fire tests were made with burning trays, either circular or square, having areas of 0.08 m^2, 0.16 m^2, 0.32 m^2, 0.64 m^2, 1.28 m^2 and 2.56 m^2. Hexane was exclusively used as fuel; it was floated on water in the trays. The preburn time was taken to be 30 seconds.

The halogenated agents employed were Halon 1011, 2402, 1301 and 1211. They were discharged through fixed spray nozzles. The application rate was measured from the variation in weight of the container. With the tests using liquid fuel, hexane, the extinction time was measured by visual observation of the flame and by means of a stop watch, while with the tests using solid combustibles, thermocouples were used

to measure the inside temperatures in order to confirm real extinction, since the sample had to be soaked for a while to cool.

The analysis of gaseous decomposition products was made by the aid of gas-chromatography for halons and carbon oxides, and the titration method for hydrogen halides.

RESULTS

The numerical data for plotting the accompanied graphical representation of the results are the average values of five runs for each class of test, except for Figures 3 and 4.

Figure 1 shows the relationship between the extinction time and the application rate of agent for hexane fires in the enclosure having a volume of 29 m^3 and with a fixed rate of ventilation.

Figure 2 shows the results of similar tests made by varying the ventilating condition and using only Halon 1011 as the extinguishing agent.

Figure 3 shows the change in temperature with time at the central portion of a wood crib for the various concentration of Halon 1301.

Figure 4 shows the change in surface temperature of burning charcoal together with the change in concentration of Halon 1301 in the enclosure.

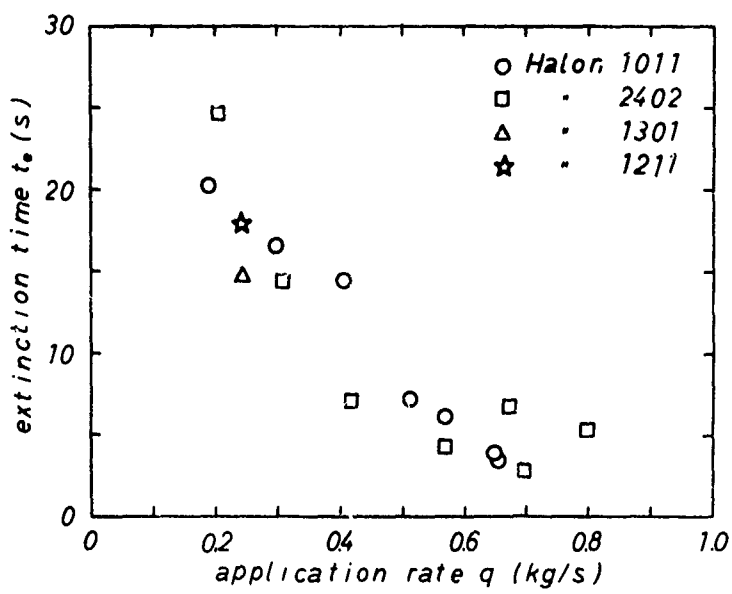

FIGURE 1. The relationship between the application rate and the extinction time for hexane fire in a 29 m^3 enclosure. The ventilation was 18 times per hour, i.e., Q = 29 x 18 m^3/hr.

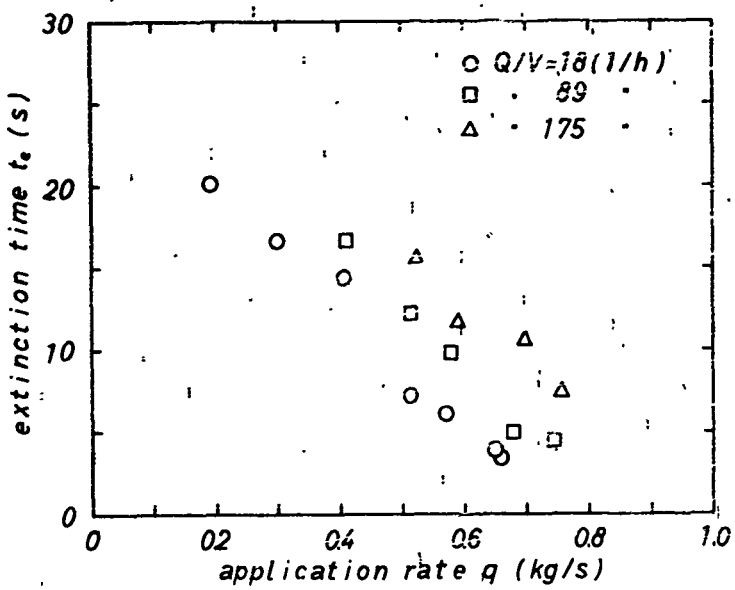

FIGURE 2. The relationship between the application rate of Halon 1011 and the extinction time for hexane fire in a 29 m^3 enclosure under different ventilation conditions.

Figure 5 shows the relationship between the extinction time with hexane fires in the open using various sizes of trays and the ratio of the application rate of Halon 1011 to the fuel evaporation rate. Figure 6 shows a similar relationship with hexane open fires in a circular tray of 64 cm in diameter and with various agents.

Figure 7 shows how the extinction time of enclosed hexane fires and the concentration of hydrogen halides change with the application rate of the agent.

As for the output of carbon monoxide during the extinction period, it was hardly dependent on the application rate of the agent, but was presumably affected by the smoldering decomposition of wooden material.

DISCUSSION

When an extinguishing agent is applied at a definite rate of application to extinguish a fire in an enclosure, which undergoes a certain constant ventilation, the manner of change in the concentration of agent between t and t+dt may be written as

$$Vdc = qdt - cQdt \qquad (1)$$

with the assumption that instant mixing and, therefore, uniform concentration are always achieved.

By integrating Eq. (1) with the initial condition c = 0 at t = 0, we get

$$t = -(V/Q)\ \ln(1-cQ/q) \qquad (2)$$

and further

$$t_c = -(V/Q)\ln(1-c_rQ/q) \qquad (3)$$

According to this equation, we know that t_c approaches infinity when q approaches c_rQ. Hence,

$$qc = c_rQ \qquad (4)$$

As for the extinction time t_e in practice, it is generally longer than t_c, i.e.,

$$t_e = t_c + t_a \qquad (5)$$

With the case of extinguishing a tray fire in the open, the dependence of the extinction time on the application rate of agent may also be expressed by the same equations as presented above, provided that suitable substitute definitions be allocated to some of the variables in the equations. That is, V should be defined as the flame volume which may be approximated by the product of the flame height and the surface area of burning liquid, and Q as the flow rate of combustible gas-mixture, which supports the flame and consists of evaporated fuel and air. This latter quantity Q is, however, generally hard to measure directly, and may rather be calculated from the air supply rate U_A or the fuel supply rate U_F by the following expressions, respectively:

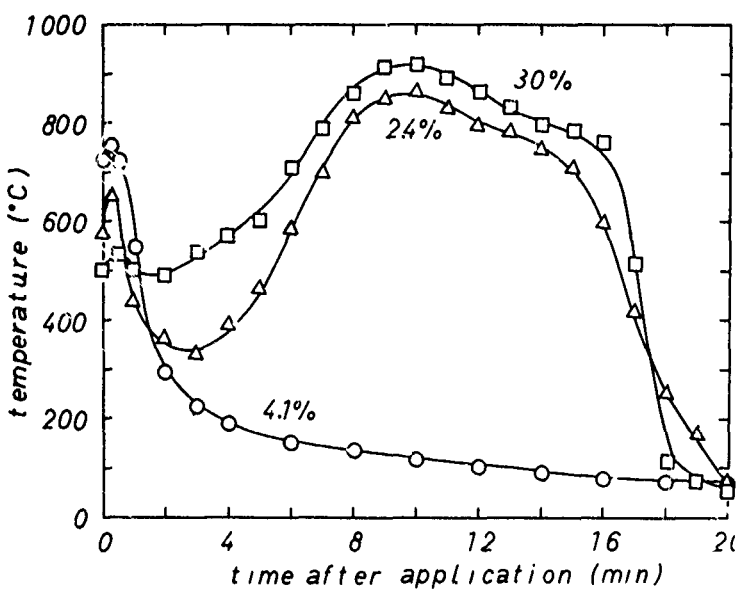

FIGURE 3. The behavior of temperatures at the center of wood crib for different concentrations of Halon 1301.

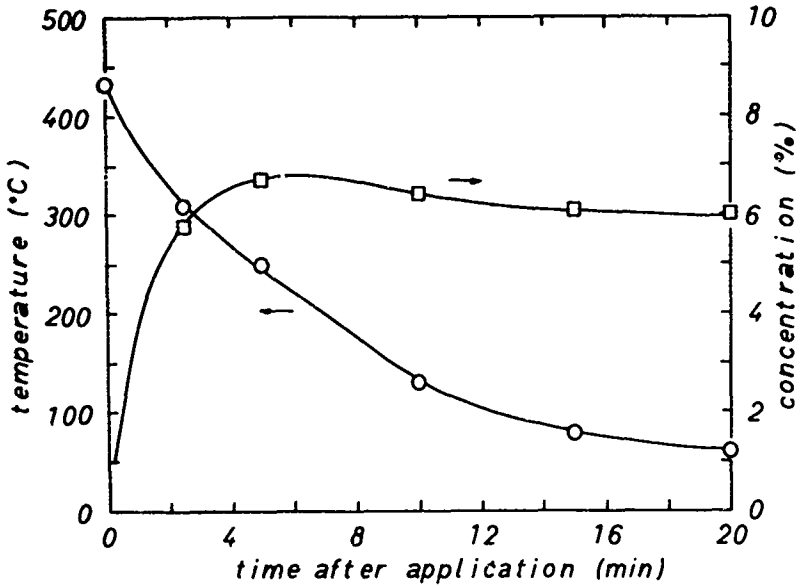

FIGURE 4. The surface temperature of charcoal and the concentration of Halon 1301 in a 2.1 m^3 enclosure expressed in terms of time.

$$Q = U_A/(1-r) \tag{6}$$

or

$$Q = U_F/r \tag{7}$$

Of these two ways for evaluating Q, the latter expression (7) is preferred, since U_F is easier to determine than U_A, i.e., U_F can be found from the burning velocity of liquid fuel. So far as the author's experiments are concerned, the ratio A/V was about 0.1 per second.

Further, the quantity q, the application rate of agent, in the case of extinguishing the open fire should be understood to represent an effective rate, i.e., the one that may directly work upon the flame, and not the one at the discharge nozzle.

The values of critical concentrations for Halons 1011, 2402, 1301, and 1211, obtained through the experiments with enclosed hexane fires, are given in the second column of Table 1, while the critical quantities for these agents with open tray fires, relative to unit volume of evaporated fuel, are given in Table 2. In both tables are given the corresponding values calculated from the data given in references cited, which were based on the explosion method or Creitz's method. It can be seen that the present experimental values are smaller than the calculated ones. Because the flames in the author's experiments are diffusion flames, it may be said that the extinguishing mechanism will differ from the case that in an explosion burette, and also that the author's experimental values are near to the values by Creitz's method.

The critical concentrations of agents with solid fuel fires, except for the case of rubber, were approximately equal to those with hexane fires, but some soaking time was needed for the combustible to cool down for complete extinction.

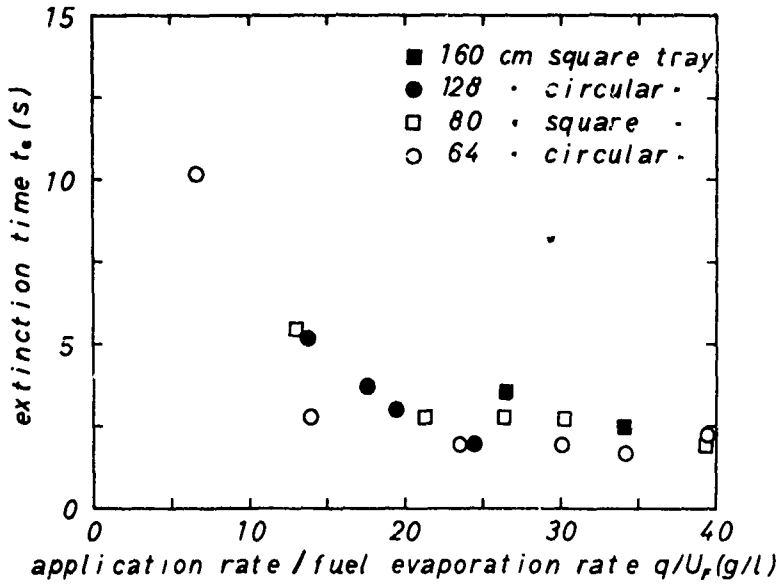

FIGURE 5. The relationship between the ratio of application rate to fuel evaporation rate and the extinction time for extinguishment of hexane fires in the open using Halon 1011.

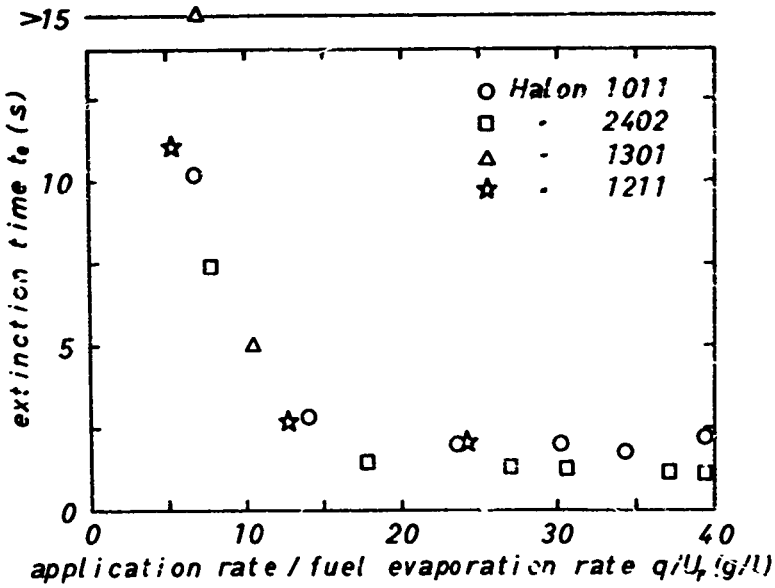

FIGURE 6. The relationship between the ratio of application rate to fuel evaporation rate and the extinction time for hexane fires in the open using various halons. The burning tray is circular with a diameter of 64 cm.

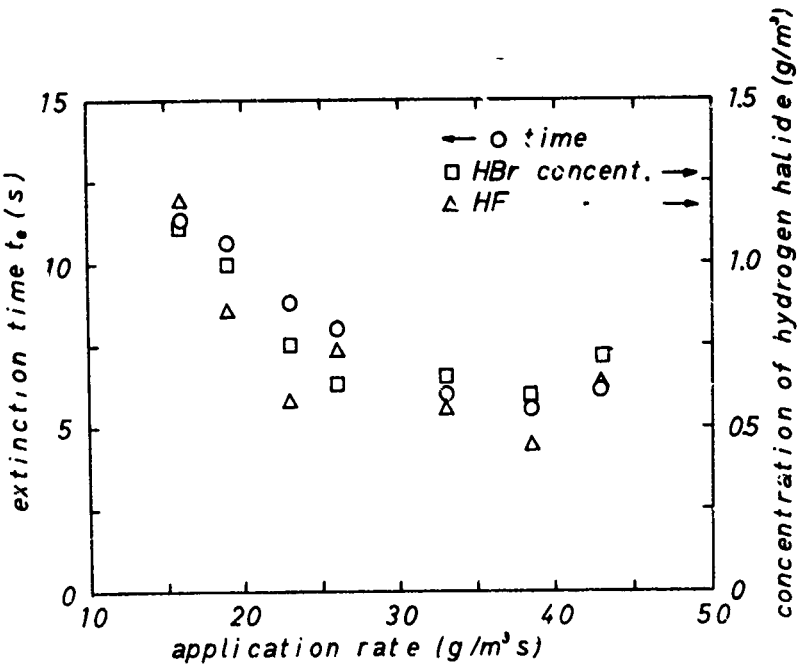

FIGURE 7. The comparison of the concentration of hydrogen halides with the extinction time in terms of the application rate.

TABLE 1

The Critical Concentration of Agent Required for the Extinguishment

Extinguishing Agent	Critical Concentration of Agent (g/m^3)		
	Experimental Value with Enclosed Fire	Calculated Value Based on References	
		Explosion Method	Creitz's Method [1]
Halon 1011	150	400 [2]	
Halon 2402	100	380 [3] 420 [4]	170 [4]
Halon 1301	120	340 [3]	
Halon 1211	150		
Carbon Dioxide	250	790	

TABLE 2

The Critical Quantity of Agent for the Extinguishment Per Unit Volume of Fuel Evaporated

Extinguishing Agent	Critical Quantity of Agent Per Unit Volume of Fuel Evaporated (g/l)	
	Experimental Value with Tray Fire in the Open	Calculated Value Based on References
Halon 1011	9.8	15.9[2]
Halon 2402	4.9	10.9[3]
Halon 1301	7.6	11.2[3]
Halon 1211	5.1	--
Carbon Dioxide	14.3	24.7

REFERENCES:

1. E. C. Creitz, J. Res. NBS 65A, 389-96, 1961.
2. E. H. Coleman, Fuel, 30, 114-115, 1951.
3. Ibid, 31:445-447, 1952.
4. N. Rainaldi, Fire Technology, 6, 59-67, 1970.

PARTICIPANTS

N. F. Alvaris, Stanford Research Institute, 333 Ravenswood Avenue, Menlo Park, California 94025

I. B. Asp, Gage-Babcock and Associates, Inc., 105 Kisco Avenue, Mt. Kisco, New York 10549

S. E. Auck, Underwriters' Laboratories, Inc., Northbrook, Illinois 60062

K. C. Back, 6570 AMRL (THT), Wright-Patterson Air Force Base, Ohio 45433

H. Ball, U.S. Forest Service, Department of Agriculture, South Agriculture Building, Washington, D.C. 20407

P. Ball, P.O. Box 7148, Ashville, North Carolina 28807

S. H. Barboo, Bureau of Medicine and Surgery, Department of the Navy, 23rd and E Streets, N.W., Washington, D.C. 20309

J. D. Bates, Fire Equipment Manufacturers' Association, Inc., 604 Davis Street, P.O. Box 1406, Evanston, Illinois 60204

M. Bauman, Rolf Jensen Associates, Inc., 540 West Frontage Road, Northfield, Illinois 60093

J. F. Bender, Maryland State Fire Marshal's Office, State Office Building, 301 West Preston Street, Baltimore, Maryland 21001

C. Bendersky, Bell Telephone Laboratories, Inc., Whippany Road, Whippany, New Jersey 07981

G. E. Benzenberg, Alison Control, Inc., P.O. Box 700, Ramsey, New Jersey 07446

W. G. Berl, Applied Physics Laboratory, The Johns Hopkins University, 8621 Georgia Avenue, Silver Spring, Maryland 20910

A. L. Berlad, Department of Engineering, State University of New York, Stony Brook, New York 11790

N. S. Bernat, American Telephone and Telegraph, 195 Broadway, New York, New York 10007

A. T. Binding, Douglas Aircraft Company, 3855 Lakewood Boulevard, Long Beach, California 90801

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B. Bischoff, Cardox, Division of Chemtron Corporation, 840 North Michigan Avenue, Chicago, Illinois 60611

J. B. Bishop, Continental Can Company, Inc., 633 Third Avenue, New York, New York 10017

R. L. Bjornsen, U.S. Forest Service, Department of Agriculture, 1621 North Kent Street, Arlington, Virginia 22209

R. E. Bland, Ordnance Research Laboratory, Pennsylvania State University, State College, Pennsylvania 16801

J. Bollinger, Southwest Research Institute, 8500 Culebra Road, San Antonio, Texas 78228

B. P. Botteri, Aero Propulsion Laboratory, Wright-Patterson Air Force Base, Ohio 45433

F. A. Bower, E. I. du Pont de Nemours & Company, Inc., P. O. Box 406, Wilmington, Delaware 19898

J. Boyle, 3198 Chestnut Street, Philadelphia, Pennsylvania 19104

J. P. Breen, D. C. Fire Department, 614 H Street, N. W., Washington, D. C. 20001

R. G. Bright, Veterans Administration, Building 225, Washington, D. C. 20234

P. C. C. Brown, Graviner Incorporated, 1121 Bristol Road, Mountainside, New Jersey 07092

R. Brown, ICI America, Inc., 24 Richmond Hill Avenue, Stamford, Connecticut 06904

J. J. Bryan, University of Maryland, College Park, Maryland 20740

E. A. Bukzin, Naval Ship Systems Command, Ship 03421, Washington, D.C. 20360

N. E. Burlinson, Naval Ordnance Laboratory, White Oak, Silver Spring, Maryland 20910

C. E. Burtner, Naval Ship Systems Command, Code 01F1, Washington, D.C. 20360

S. E. Bush, Library of Congress, 10 First Street, S. W., Washington, D. C. 20540

D. Call, Naval Air Station, Miramar, California 92145

R. G. Canning, Canadian Armed Forces Fire Marshal's Office, Hunter Building, Ottawa, Ontario KIA OK2

J. G. Carlisle, Corpus Christi Fire Department, 1401 Morgan, Corpus Christi, Texas 78404

H. Carhart, Naval Research Laboratory, Code 6180, Washington, D. C. 20390

J. T. Carr, Marine Corps Development Center, Quantico, Virginia 22134

W. G. Carson, Potomac Electric Power Company, 929 E Street, N. W., Washington, D. C. 20004

H. E. Christensen, National Institute of Occupational Safety and Health, 5600 Fishers Lane, Rockville, Maryland 20852

W. J. Christian, Underwriters' Laboratories, Inc., 333 Pfingsten Road, Northbrook, Illinois 60062

D. G. Clark, Imperial Chemical Industrial Hygiene Research Laboratories, Alderley Park, North Macclesfield, Cheshire, England

R. A. Cliffe, Committee on Fire Research, National Academy of Sciences, Washington, D. C. 20418

R. E. Collins, Johnson and Higgins of Virginia, Inc., P. O. Box 1137, Richmond, Virginia 23208

J. J. Comeford, National Bureau of Standards, U.S. Department of Commerce, Washington, D. C. 20234

T. H. Curry, E. I. du Pont de Nemours & Company, Inc., 9 Germay Drive, Wilmington, Delaware 19898

R. J. Daley, American Electric Power Service Corporation, 2 Broadway, New York, New York 10004

G. H. Damon, Bureau of Mines, U.S. Department of Interior, Washington, D. C. 20240

R. L. Darwin, Naval Materiel Command, Department of the Navy, Washington, D. C. 20360

W. E. DeGrafft, Naval Ship Research and Development Center, Annapolis, Maryland 21402

J. Dehn, Ballistic Research Laboratory, Aberdeen Proving Ground, Maryland 21005

J. R. DeMonbrun, Union Carbide Corporation, Oak Ridge, Tennessee 37830

C. A. Doak, Alison Control, Inc., P. O. Box 700, Ramsey, New Jersey 07446

H. Dorl, Ore & Chemical Corporation, 235 East 42 Street, New York, New York 10017

V. A. Dorr, Union Carbide Corporation, Tarrytown, New York 10591

A. W. DuBrul, U. S. Coast Guard, Department of Transportation, Washington, D. C. 20591

C. J. Eby, Monsanto Company, 1101 17 Street, N.W., Washington, D.C. 20036

R. E. Eckhardt, Esso Research and Engineering Company, Linden, New Jersey 07036

G. S. Economy, Norton Air Force Base, San Berardino, California 92409

A. Edmonds, Imperial Chemical Industries Limited, Mond Division, Runcorn, Cheshire, England

I. N. Einhorn, College of Engineering, University of Utah, Salt Lake City, Utah 84112

H. V. Ellis, Walter Reed Army Medical Center, Washington, D.C. 20012

T. S. Ely, Eastman Kodak Company, Kodak Park, Rochester, New York 14650

R. C. Ertel, Liberty Mutual Insurance Company, Bala Cynwyd, Pennsylvania 19004

M. H. Estipp, Prince George's County Fire Department, Brentwood, Maryland 20722

R. C. Everson, Marsh and McLennan Protection Consultants, 70 Pine Street, New York, New York 10005

N. L. Fannick, Bureau of Mines, Department of Interior, Washington, D. C. 20240

D. C. Fariss, E. I. du Pont de Nemours & Company, Inc., 9 Germay Drive, Wilmington, Delaware 19898

M. Feldman, The Sierra Group, P. O. Box 158, Santa Barbara, California 93102

G. H. Fielding, Naval Research Laboratory, Washington, D. C. 20390

R. J. Finnerty, American Telephone and Telegraph Company, 195 Broadway, New York, New York 10007

J. Floria, E. I. du Pont de Nemours & Company, Inc., P. O. Box 406, Wilmington, Delaware 19898

C. L. Ford, E. I. du Pont de Nemours & Company, 1331 Farmers Bank Building, Wilmington, Delaware 19898

T. E. Franck, Argonne National Laboratories, 9700 South Cass Avenue, Argonne, Illinois 60440

S. L. Friess, National Naval Medical Center, Bethesda, Maryland 20014

K. L. Gabriel, Medical College of Pennsylvania 3300 Henry Avenue, Philadelphia, Pennsylvania 19129

R. Gasi, Chemore Corporation, 100 East 42 Street, New York, New York 10017

J. J. Gassmann, Federal Aviation Agency, Atlantic City, New Jersey 08405

L. H. Gevantman, National Bureau of Standards, Department of Commerce, Washington, D. C. 20234

C. Goll, 6314 Gentele Court, Alexandria, Virginia 22310

T. E. Goonan, General Services Administration, 7th and D Streets, S. W., Washington, D. C. 20407

J. P. Goudreau, The Ansul Company, One Stanton Street, Marinette, Wisconsin 54143

G. J. Grabowski, Fenwal Incorporated, Ashland, Massachusetts 01721

H. H. Green, Honeywell Corporation, P. O. Box 6000, Phoenix, Arizona 85005

T. B. Griffin, Albany Medical College of Union University, New Scotland Avenue, Albany, New York 12208

J. M. Hammock, National Fire Protection Association, 60 Batterymarch Street, Boston, Massachusetts 02110

W. L. Hanbury, National Aeronautics and Space Administration, 6th and Maryland Avenue, S. W., Washington, D. C. 20546

J. W. Hannan, New York Port Authority Police Academy, 325 Spring Street, New York, New York 10013

D. J. Harris, Naval Air Test Center, Patuxent River, Maryland 20670

E. S. Harris, NASA Manned Spacecraft Center, Houston, Texas 77058

W. S. Harris, The Abraham Lincoln School of Medicine, University of Illinois Hospital, Chicago, Illinois 60680

E. E. Harton, Department of Transportation, Washington, D. C. 20590

C. E. Hathaway, Monsanto Industrial Chemicals Company, 800 North Lindbergh, St. Louis, Missouri 63166

H. W. Hays, Agricultural Research Service, Department of Agriculture, Washington, D. C. 20250

J. R. Henry, Combat Developments Command, Fort Belvoir, Virginia 22060

R. J. Hershman, Department of the Navy, Norfolk, Virginia 23511

L. B. Hicks, Federal Fire Council, 7th and D Streets, S. W., Washington, D. C. 20407

J. W. Hiddemen, TRW Hazleton Laboratories, 9200 Leesburg Turnpike, Vienna, Virginia 22180

T. Hill, National Naval Medical Center, Bethesda, Maryland 20014

A. H. Hobelmann, Walter Kidde and Company, 14506 Faraday Drive, Rockville, Maryland 20853

N. Hoogmoed, Alison Control Incorporated, P. O. Box 700, Ramsey, New Jersey 07446

T. G. Horeff, Federal Aviation Agency, 800 Independence Avenue, S. W., Washington, D. C. 20591

R. J. M. Horton, National Environment Research Center, Research Triangle Park, North Carolina 27711

R. B. Howard, Buffalo Fire Department, 2401 City Hall, Buffalo, New York 14222

C. Huggett, National Bureau of Standards, Department of Commerce, Washington, D. C. 20234

C. W. Irwin, 336 Mt. Hope Avenue, Bangor, Maine 04401

E. J. Jablonski, Naval Research Laboratory, Washington, D. C. 20390

D. F. Janes, Oklahoma State University, Stillwater, Oklahoma 74074

R. Jensen, Illinois Institute of Technolcgy, Chicago, Illinois 60616

E. B. Jones, Naval Air Station, Norfolk, Virginia 23503

O. W. Jones, Department of the Air Force, HQ USAF'SGAAP, Washington, D. C. 20314

T. Jones, Oklahoma State University, Stillwater, Oklahoma 74074

A. S. Kalelkar, Arthur D. Little, Inc., 20 Acorn Park, Cambridge, Massachusetts 02140

F. Kamowski, Norris Industries, P. O. Box 2750, Newark, New Jersey 07114

W. R. Kane, Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio 45433

D. Kay, Naval Ship Engineering Center, Hyattsville, Maryland 20782

C. Kenney, United States Capitol, Washington, D. C. 20515

J. W. Kerr, Office of Civil Defense, Department of Defense, The Pentagon, Washington, D. C. 20310

L. G. Kirk, E. I. du Pont de Nemours & Company, Inc., 9 Germay Drive, Wilmington, Delaware 19898

D. B. Knowles, United States Capitol, Washington, D. C. 20515

J. M. Kuchta, Pittsburgh Mining and Safety Research Center, Bureau of Mines, Pittsburgh, Pennsylvania 15213

R. H. Lang, National Aeronautics and Space Administration, Washington, D. C. 20546

C. N. La Rosa, Naval Ship Research and Development Center, Annapolis, Maryland 21402

E. R. Larsen, Dow Chemical Company, 768 Building, Midland, Michigan 48640

K. F. Lawler, Fire Department, 2130 Oakridge Avenue, Madison, Wisconsin 53704

G. M. Lawton, Bureau of Medicine and Surgery, Department of the Navy, Washington, D. C. 20390

F. J. Lemmer, U. S. Army Tank-Automotive Command, 28251 Van Dyke, Warren, Michigan 48090

H. Leppke, Air Line Pilots Association, 501 North Waiola, LaGrange Park, Illinois 60525

W. Ligon, 2701 Briggs-Chaney Road, Silver Spring, Maryland 20904

R. H. Long, National Science Foundation, Washington, D. C. 20550

J. C. Loria, National Aeronautics and Space Administration, Washington, D. C. 20546

F. B. Lovell, Naval Ship Engineering Center, Hyattsville, Maryland 20782

J. D. MacEwen, SysteMed Corporation, P. O. Box 3067, Dayton, Ohio 45431

D. J. MacKay, Advanced Safety Systems, Inc., 620 Massachusetts Avenue, Cambridge, Massachusetts 02139

D. Maddock, Safety First Products Corporation, 175 Sawmill River Road, Elmsford, New York 10523

M. W. Magee, Lawrence Livermore Laboratory, Livermore, California 94550

W. F. Malone, Environmental Protection Agency, 330 Independence Avenue, S. W., Washington, D. C. 20201

W. W. Maybee, Atomic Energy Commission, Washington, D. C. 20545

R. B. McCann, Naval Ship Engineering Center, Hyattsville, Maryland 20782

R. E. McComb, Library of Congress, Washington, D. C. 20540

D. E. McDaniel, U. S. Coast Guard, Washington, D. C. 20590

E. T. McHale, Atlantic Research Corporation, Shirley Highway at Edsall Road, Alexandria, Virginia 22314

G. W. McKenzie, Trans World Airlines, Inc., Kansas City International Airport, Kansas City, Missouri 64153

J. E. McLinn, The Sierra Group, P. O. Box 158, Santa Barbara, California 93102

W. J. McNamara, U. S. Army Engineering Research and Development Center, Fort Belvoir, Virginia 22060

R. C. Merritt, Factory Mutual Research Corporation, 1151 Boston-Providence Turnpike, Norwood, Massachusetts 02062

M. J. Miller, Factory Mutual Research Corporation, 1151 Boston-Providence Turnpike, Norwood, Massachusetts 02062

R. Mitton, Pyrotector, Inc., 1401 Wilson Boulevard, Arlington, Virginia 22209

L. R. Morcone, Maryland Fire Equipment Corporation, 12284 Wilkins Avenue, Rockville, Maryland 20852

J. F. Morehead, Union Carbide Corporation, P. O. Box Y, Oak Ridge, Tennessee 37830

W. Morgan, Walter Kidde and Company, 675 Main Street, Belleville, New Jersey 07109

W. W. Morgan, Pennwalt Corporation, Penwalt Building, Philadelphia, Pennsylvania 19102

H. H. Murdock, Birmingham Fire Department, 4825 Avenue W, Birmingham, Alabama 35208

G. T. Murray, American Airlines, Inc., LaGuardia Airport, Flushing, New York 11371

T. G. Neff, Bovay Engineers, Inc., 5009 Caroline Street, Houston, Texas 77004

R. Neill, Naval Research Laboratory, Washington, D. C. 20390

L. Northcutt, U. S. Forest Service, Department of Agriculture, Washington, D. C. 22050

D. M. O'Brien, International Association of Fire Chiefs, 232 Madison Avenue, New York, New York 10016

R. C. Olsen, Allied Chemical Corporation, P. O. Box 1057R, Morristown, New Jersey 08960

J. F. O'Regan, Feecon Corporation, 515 Washington Street, Auburn, Massachusetts 01501

W. B. Pacheco, U. S. Coast Guard, Department of Transportation, Washington, D. C. 20590

T. Y. Palmer, U. S. Forest Service, Department of Agriculture, Riverside, California 92507

J. A. Parker, Ames Research Center, National Aeronautics and Space Administration, Mountain View, California 94035

J. W. Parris, Asheville Fire Department, Municipal Building, Asheville, North Carolina 28807

J. V. Peck, Parker-Hannifin Corporation, 18321 Jamboree Boulevard, Irvine, California 82664

R. C. Perry, Reynolds Electrical and Engineering Company, Inc., P. O. Box 14400, Las Vegas, Nevada 89114

H. B. Peterson, Naval Research Laboratory, Washington, D. C. 20390

P. Peterson, Fenwal Incorporated, 400 Main Street, Ashland, Massachusetts 01721

P. E. Phillips, Atomic Energy Commission, P. O. Box 14100, Las Vegas, Nevada 89114

I. I. Pinkel, Lewis Research Center, National Aeronautics and Space Administration, Cleveland, Ohio 44135

W. J. Plummer, National Bureau of Standards, Department of Commerce, Gaithersburg, Maryland 20234

A. B. Poch, UNIVAC, Division of Sperry Rand Corporation, Roseville, Minnesota 55113

T. G. Provenzano, Office of Civil Defense, Department of Defense, The Pentagon, Washington, D. C. 20310

J. E. Pruitt, Parker-Hannifin Corporation, 14113 Heritage Lane, Silver Spring, Maryland 20806

N. Rainaldi, Montecatini-Edison, Electricita 41, Stabilimento Petrolchimico, Porto Marghera, Italy

W. W. Ranson, E. I. du Pont de Nemours & Company, Inc., 9 Germay Drive, Wilmington, Delaware 19898

R. L. Reichard, International Business Machines, 8027 Leesburg Pike, McLean, Virginia 22101

R. J. Reilly, Jaros, Baum and Bolles, 345 Park Avenue, New York, New York 10022

C. F. Reinhardt, E. I. du Pont de Nemours & Company, Inc., Haskell Laboratory, Newark, Delaware 19711

L. H. Reinke, E. I. du Pont de Nemours & Company, Inc., 9 Germay Drive, Wilmington, Delaware 19898

R. A. Rhoden, Environmental Protection Agency, 5600 Fishers Lane, Rockville, Maryland 20852

W. L. Richardson, Union Carbide Corporation, P. O. Box P, Oak Ridge, Tennessee 37830

J. F. Riley, The Ansul Company, One Stanton Street, Marinette, Wisconsin 54143

R. B. Roberts, Rhodia Incorporated, 600 Madison Avenue, New York, New York 10022

A. F. Robertson, National Bureau of Standards, Department of Commerce, Washington, D. C. 20234

M. M. Robsion, Applied Physics Laboratory, The Johns Hopkins University, Silver Spring, Maryland 20910

J. Rockett, National Bureau of Standards, Department of Commerce, Washington, D. C. 20234

C. M. Rollhauser, Naval Ship Research and Development Center, Annapolis, Maryland 21402

M. J. Romanell, Materiel Testing Directorate, Aberdeen Proving Ground, Maryland 21005

E. J. Rozniecki, U. S. Army Tank-Automotive Command, 28215 Van Dyke, Warren, Michigan 48090

G. W. Savocool, Environmental Protection Agency, Route D, North Carolina 27701

D. R. Sayers, ICI America, Inc., 24 Richmond Hill Avenue, Stamford, Connecticut 06904

W. E. Scheimann, National Loss Control Service Corporation, Long Grove, Illinois 60049

T. H. Seymour, Occupational Safety and Health Act, 400 1st Street, N. W., Washington, D. C. 20210

D. F. Sheehan, U. S. Coast Guard, Department of Transportation, Washington, D. C. 20591

J. R. Shenk, The Prudential Insurance Company of America, Prudential Plaza, Newark, New Jersey 07101

R. E. Shiels, Improved Risk Mutuals, 15 North Broadway, White Plains, New York 10601

V. A. Sielert, General Telephone and Electronics Corporation, 730 Third Avenue, New York, New York 10017

O. M. Slye, Mobil Research and Development Corporation, P. O. Box 1026, Princeton, New Jersey 08540

H. D. Smith, Texas A & M University, College Station, Texas 77843

H. L. Smith, Columbia Union College, Takoma Park, Maryland 20012

D. E. Snowdon, Fenwal Incorporated, P. O. Box 439, Annandale, Virginia 22003

E. J. Soltis, Walter Kidde and Company, 675 Main Street, Belleville, New Jersey 07109

A. Speigelman, American Insurance Association, 85 John Street, New York, New York 10038

E. M. Sporn, U. S. Army Research Office, 3045 Columbia Pike, Arlington, Virginia 22204

M. Steinberg, U. S. Army Environmental Hygiene Agency, Aberdeen Proving Ground, Maryland 21010

R. D. Stewart, Medical College of Wisconsin, Milwaukee, Wisconsin 53226

H. E. Stokinger, National Institute of Occupational Safety and Health, 1014 Broadway, Cincinnati, Ohio 45202

M. Suchomel, 18724 Walder's Choice Road, No. 6, Gaithersburg, Maryland 20760

K. Sumi, National Research Council, Ottawa, Canada KIA-OR6

R. F. Sunstrom, The Ansul Company, One Stanton Street, Marinette, Wisconsin 54143

R. D. Sykes, National Aeronautics and Space Administration, Kennedy Space Center, Florida 32899

R. P. Sylvia, Fire Engineering Magazine, 466 Lexington Avenue, New York, New York 10017

L. E. Tarbell, Federal Aviation Administration, Department of Transportation, 800 Independence Avenue, Washington, D. C. 20590

H. L. Theis, The Ansul Company, One Stanton Street, Marinette, Wisconsin 54143

G. W. Thomas, Liberty Mutual Loss Prevention, 10 Rockefeller Plaza, New York, New York 10020

J. F. Thomas, University of California, Berkeley, California 94720

H. Tipton, National Commission on Fire Prevention and Control, 1730 K Street, N. W., Washington, D. C. 20006

T. R. Torkelson, The Dow Chemical Company, 9008 Building, Midland, Michigan 48640

R. Transue, Pyrotronics Corporation, 8 Ridgedale Avenue, Cedar Knolls, New Jersey 07005

R. F. Trump, Alison Control Incorporated, P. O. Box 700, Ramsey, New Jersey 07446

D. B. Tucker, Factory Insurance Association, 85 Woodland Street, Hartford, Connecticut 06102

R. L. Tuve, Applied Physics Laboratory, The Johns Hopkins University, Silver Spring, Maryland 20910

M. Tyler, Aircraft Ground Fire Suppression and Rescue System, Wright-Patterson Air Force Base, Ohio 45433

J. H. Uliana, Bethlehem Steel Corporation, 500 West Office Building, Bethlehem, Pennsylvania 18016

C. H. Van Vierssen, Embassy of the Netherlands, Washington, D. C. 20008

V. Visbeck, Mobil Equipment Research and Development Center, Fort Belvoir, Virginia 22060

C. W. Volkamer, Chicago Fire Academy, 558 West DeKoven Street, Chicago, Illinois 60607

J. P. Wagner, Factory Mutual Research Corporation, 1151 Boston-Providence Turnpike, Norwood, Massachusetts 02339

C. W. Walter, Harvard Medical School, Boston, Massachusetts 02110

R. C. Wands, Committee on Toxicology, National Academy of Sciences, Washington, D. C. 20418

W. D. Weatherford, Southwest Research Institute, San Antonio, Texas 78284

H. R. Wesson, University of Oklahoma, Norman, Oklahoma 73069

E. Whittington, U. S. Army Materiel Command, Washington, D. C. 20315

R. T. Wickham, Wickham Associates, 1395 Main Street, Marinette, Wisconsin 54143

H. V. Williamson, Cardox Division, Chemtron Corporation, 840 North Michigan Avenue, Chicago, Illinois 60611

R. B. Williamson, University of California, Berkeley, California 84720

R. Wilson, FIREPRO Incorporated, P. O. Box 145, Wellesley Hills, Massachusetts 02181

C. J. Winquist, Gage-Babcock and Associates, Inc., 105 Kisco Avenue, Mt. Kisco, New York 10549

M. Wismer, PPG Industries, One Gateway Center, Pittsburgh, Pennsylvania 15200

L. R. Woltz, Fire Department, Prince George's County, Brentwood, Maryland 20722

W. S. Wood, Sun Oil Company, P. O. Box 426, Marcus Hook, Pennsylvania 19061

R. A. Wright, Fire Department, Village of LaGrange, LaGrange, Illinois 60525

R. J. Wright, Underwriters' Laboratories of Canada, Seven Crouse Road, Scarborough, Ontario, Canada

F. Yocum, D. C. Fire Department, 4600 Overlook Avenue, S. W., Washington, D. C. 20032

C. H. Yuill, Southwest Research Institute, 8500 Culebra Road, San Antonio, Texas 78228

B. A. Zikria, Columbia-Presbyterian Medical Center, New York, New York 10032

K. Zuber, Walter Kidde and Company, Inc., 675 Main Street, Belleville, New Jersey 07109

F. R. Zumbro, E. I. du Pont de Nemours & Company, Inc., 1333 Farmers Bank Building, Wilmington, Delaware 19898