ESL-TR-86-17

Extinguishing Agent for Magnesium Fire: Phases I–IV

ROBERT E. TAPSCOTT
HAROLD D. BEESON
MICHAEL E. LEE
MARTIN A. PLUGGE
DENNIS M. ZALLEN
JOSEPH L. WALKER
PHYLLIS CAMPBELL

NEW MEXICO ENGINEERING
RESEARCH INSTITUTE
BOX 25
UNIVERSITY OF NEW MEXICO
ALBUQUERQUE NM 87131

JULY 1986

FINAL REPORT

JANUARY 1985 - JANUARY 1986

APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED

AFESC

ENGINEERING & SERVICES LABORATORY
AIR FORCE ENGINEERING & SERVICES CENTER
TYNDALL AIR FORCE BASE, FLORIDA 32403

NAVAIR

NAVAL AIR SYSTEMS COMMAND
DEPARTMENT OF NAVY,
WASHINGTON DC 20361

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION
UNCLASSIFIED

1b. RESTRICTIVE MARKINGS

2a. SECURITY CLASSIFICATION AUTHORITY

2b. DECLASSIFICATION / DOWNGRADING SCHEDULE

3. DISTRIBUTION / AVAILABILITY OF REPORT
Approved for public release;
Distribution unlimited.

4. PERFORMING ORGANIZATION REPORT NUMBER(S)
NMERI WA3-15 (S.S. 3.07)

5. MONITORING ORGANIZATION REPORT NUMBER(S)
ESL-TR-86-17

6a. NAME OF PERFORMING ORGANIZATION
New Mexico Engineering
Research Institute

6b. OFFICE SYMBOL *(If applicable)*
NMERI

7a. NAME OF MONITORING ORGANIZATION
Engineering and Services Laboratory

6c. ADDRESS *(City, State, and ZIP Code)*
Box 25, University of New Mexico
Albuquerque, New Mexico 87131

7b. ADDRESS *(City, State, and ZIP Code)*
Air Force Engineering and Services Center
Tyndall Air Force Base, Florida 32403

8a. NAME OF FUNDING / SPONSORING ORGANIZATION
AFESC/RD and NAVAIR

8b. OFFICE SYMBOL *(If applicable)*

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
Contract No F29601-84-C-0080

8c. ADDRESS *(City, State, and ZIP Code)*
(AIR FORCE) - Tyndall AFB FL 32403
(NAVAIR) - Washington DC 20361

10. SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.
6327F	2104	10	33

11. TITLE *(Include Security Classification)*
EXTINGUISHING AGENT FOR MAGNESIUM FIRE: PHASES I-IV

12. PERSONAL AUTHOR(S)
Robert E. Tapscott, Harold D. Beeson, Michael E. Lee, Martin A. Plugge, (OVER)

13a. TYPE OF REPORT
FINAL

13b. TIME COVERED
FROM 8501 TO 8601

14. DATE OF REPORT *(Year, Month, Day)*
July 1986

15. PAGE COUNT
222

16. SUPPLEMENTARY NOTATION
Availability of this report is specified on reverse of front cover.

17. COSATI CODES

FIELD	GROUP	SUB-GROUP
06	07	
11	06	

18. SUBJECT TERMS *(Continue on reverse if necessary and identify by block number)*
Fire Suppression (Metal Fires), Fire Extinguisher (Class D)

19. ABSTRACT *(Continue on reverse if necessary and identify by block number)*

This report evaluates the effectiveness of existing extinguishing agents for metal fires. Testing of new and modified extinguishing agents for general configuration proved suppression and extinguishing capabilities. Therefore, extensions of existing agents via addition/reformulations were evaluated. As a result of these evaluations, an effective metal fire extinguishing system was developed. Preliminary large-scale tests were conducted and the performance of the system was evaluated.

20. DISTRIBUTION / AVAILABILITY OF ABSTRACT
☐ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS

21. ABSTRACT SECURITY CLASSIFICATION
UNCLASSIFIED

22a. NAME OF RESPONSIBLE INDIVIDUAL
JOSEPH L. WALKER

22b. TELEPHONE *(Include Area Code)*
(904) 283-6194

22c. OFFICE SYMBOL
HQ AFESC/RDCF

DD FORM 1473, 84 MAR

83 APR edition may be used until exhausted.
All other editions are obsolete.

12. PERSONAL AUTHOR(S) (CONCLUDED)

Dennis M. Zallen, Joseph L. Walker, and Phyllis Campbell.

PREFACE

This report was prepared by the New Mexico Engineering Research Institute (NMERI), University of New Mexico, Campus Box 25, Albuquerque, New Mexico 87131, under Contract Number F29601-84-C-0080, for the Air Force Engineering and Services Center, Engineering and Services Laboratory (AFESC/RDCF), Tyndall Air Force Base, Florida 32403, and the Naval Air Systems Command (NAVAIR), Washington, DC 20361.

This report summarizes work done between 14 January 1985 and 31 January 1986. HQ AFESC/RDCF program manager was Joseph L. Walker, and NAVAIR Fire Protection Technical Manager was Phyllis Campbell.

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

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

JOSEPH L. WALKER
Program Manager

James R. VanOrman
JAMES R. VAN ORMAN
Deputy Director of Engineering
and Services Laboratory

Everett L. Mabry
EVERETT L. MABRY, Colonel, USAF
Chief, Engineering Research Division

(The reverse of this page is blank.)

TABLE OF CONTENTS

TABLE OF CONTENTS (CONCLUDED)

LIST OF FIGURES

LIST OF FIGURES (CONCLUDED)

LIST OF TABLES

(The reverse of this page is blank.)

SECTION I
INTRODUCTION

OBJECTIVE

The objective of this effort is to extend, develop, or originate an extinguishing agent to combat magnesium fires.

BACKGROUND

A number of very costly incidents have occurred that exemplify the importance of configuration and type of burning material in fire suppression. One recent incident was a C-5A engine fire at Altus Air Force Base (AFB), Oklahoma. The overall fire was controlled by mass applications of Aqueous Film-Forming Foam (AFFF). A small unit of a Class D agent was available but ineffective for the vertical configuration involved. Other examples of unsuppressed burning caused by configuration and/or material type providing continuous ignition to normally extinguished fires included a B-52 fire at Grand Forks AFB in September 1980, a C-141 fire at Charleston AFB in September 1979, and an EC-135 fire at Langley AFB in January 1980.

The development of firefighting agents has been oriented toward agents needed to extinguish the majority of fuels--primarily liquid propulsion fuels and cellulosic materials. A general extinguishing agent does not exist for metal fires, especially those involving magnesium in configurations not directly accessible or in suspended, vertical orientations.

SCOPE

The scope of this task involves the evaluation of existing extinguishing agents for metal fires as to their applicability to general configurations. Extensions of existing agents via addition/reformulations are evaluated. If existing agents cannot be made acceptable, new compounds will be sought. Testing of new and modified extinguishing agents for general-configuration metal fires will prove suppression and extinguishing capabilities. The final product of this effort will be a technical report detailing all work accomplished, conclusions, recommendations, and a draft specification to procure the extinguishing agent to be delivered in a separate report.

NOMENCLATURE

Halons are halogenated hydrocarbons. When used generically, the word "halon" remains uncapitalized; however, when used as part of a designation for a specific compound, e.g., Halon 1211 or Halon 2402, it is capitalized.

SECTION II

PHASE I--EVALUATION OF EXISTING AGENTS

TASKS FOR PHASE I

In Phase I, existing extinguishing agents for metal fires shall be identified and their properties and compositions noted. Performance tests shall be conducted. Literature pertaining to the nature of metal fires and their combustion and extinction mechanisms shall also be documented. Based on the results of this effort, a recommendation shall be made on how to best accomplish the end result of a general-configuration metal fire-extinguishing agent.

BURNING AND EXTINGUISHMENT

A generalized description of burning and extinguishment is presented in this section. A review of the extinguishment of burning solids is then presented. The summary of thermophysical models for the burning of magnesium is followed by a review of the homogeneous reaction kinetics for magnesium. These fundamentals help in understanding and evaluating the burning and extinguishment of magnesium during the origination and/or development of an extinguishing agent to combat magnesium fires.

Basics of Fire Extinguishment

A fire is simply the balance of heat input versus heat loss, Q_{in} versus Q_{out}. If Q_{out} is greater than Q_{in}, the fire goes out. The initial Q_{in} is provided by an igniter, such as a match. If a fire is started by the igniter, the Q_{in} is provided by the reaction in the fire. This reaction is usually a fuel being oxidized by the oxygen in the air. Some fuels which react to produce heat (exothermic reaction) do not involve oxygen; however, these are fewer than those involving air oxidation of a fuel to produce energy.

A fire will be extinguished when Q_{out} is greater than Q_{in}. Several factors contribute to Q_{in}. One important factor is the heat release from the chemical reactions that occur at a certain rate. The rate of a chemical reaction increases as the concentration of the reactants (fuel and oxidizer species) increase and as the temperature is increased. Another important factor is the radiation and conduction from the flame front. These are transmitted to the fuel surface to heat the fuel so that it is released toward the flame front, where it reacts with the oxidant. Knowing the basic factors that compose Q_{in} leads to several means of extinguishing a flame by lowering Q_{in} and relatively increasing Q_{out}.

The various approaches to the practical problem of extinguishing fires can be categorized as follows:

1. Isolate the fuel.
2. Isolate the oxidizer.
3. Cool condensed fuels.
4. Cool the gas phase.
5. Blow away the flame.
6. Inhibit chemical reaction homogeneously.
7. Inhibit chemical reaction heterogeneously.

The means by which fires can be extinguished may be broadly subdivided into physical mechanisms, Categories 1-5; and chemical mechanisms, Categories 6 and 7. The action of extinguishing agents which are in practical use and which may simultaneously involve several of the categorical effects are discussed below.

Physical Extinguishment

If a fire is of the nonpremixed type, it can be extinguished by separating the reactants with an inert blanket. This mechanism operates with gas, liquid, and solid extinguishers to a greater or lesser degree; but is particularly important in the case of foams. The principal function of foam for extinguishing liquid fuel fires is the isolation of the fuel by forming a relatively long-lived blanket. The foam also cools the condensed and, perhaps, gaseous phases; but the reduction in the reactant concentration is the primary mode of operation. If air is the foaming gas, then the water film and its additives must be the active agents of suppression. On the other hand, if the foaming gas is noncombustible, the foam film acts as a barrier to retain the blanket of inert gas. It appears obvious, and has been confirmed experimentally, that inert gas foam is more effective than an air foam. An addition to the reactant separator category has been surfactants, that is, surface active agents which form a monomolecular or thicker layer over a burning liquid, reducing its vapor pressure below the flammability limit. The combination of such agents with foam and powder is particularly effective.

A common method of extinguishing a fire is to blanket it with an inert gas. Carbon dioxide and nitrogen gases extinguish flames chiefly by their blanketing effect, which isolates the oxidizer. Many substances which are essentially inert under usual fire conditions may become reactive under unusual conditions. For instance, CO_2 and H_2O contain oxygen, which may be extracted and used as the oxidant under very high temperature or very reactive conditions.

As with most extinguishment techniques, several processes are important in fire suppression; and it is often impossible to separate them or isolate the dominant processes which may vary from case to case. With CO_2 extinguishers, the material is added in the form of low-temperature snow, and the action can be manifold. The gas will dilute and lower flame temperatures. The heat of sublimation of the CO_2 is appreciable; and this result lowers the flame temperature. The solid particles can fall into a burning liquid pool, producing a froth of cold bubbles which reduces the vapor pressure of the liquid through the combined actions of cooling and evaporation, bringing the liquid below the flash point. The jet of cold gas may produce such steep velocity gradients that the fire is blown out. Finally, the gas provides an inert blanket separating the burning fuel from the surrounding oxidizer. Carbon tetrachloride and methyl bromide likewise exert a blanketing effect in their application to fires. Additives may be used to decrease the runoff by increasing viscosity and by forming a reflecting barrier over the burning surface reducing the radiant heat transfer.

The most effective mode of action of water as a fire suppressant is to cool condensed fuels. Firefighters usually are instructed to apply water to the condensed phase, not to the flame. In addition to achieving extinction, this helps to prevent reignition. The application of agents to the liquid or solid fuel can cool it sufficiently so that the vapor pressure of the liquid and, hence, the rate of supply of combustible vapor to the flame zone will be diminished to the point where the fire will be extinguished. The characteristics of fire-extinguishing agents that contribute to the effective cooling properties are high heat capacity, high rate of vaporization, and the ability to undergo endothermic decomposition.

Water and fog nozzles might also achieve extinction by cooling the gas-phase flames, but this mechanism is less efficient (amount of agent required) than cooling the fuel. A principal action of a liquid is to extract heat from the fire through its latent heat of vaporization and heat capacity. From this standpoint, water is a uniquely suitable liquid. It is stable, noncombustible and nontoxic with a high heat of vaporization. Auxiliary effects of these liquids are the diluent and blanket actions. Heat extraction from a flame system reduces flame temperatures. This sharply reduces the reaction rates which depend exponentially on temperature. This can be an important effect in fire extinction by powders, though it is usually of secondary importance compared with chemical effects. Heat extraction by powders is limited by their heat capacities and emissivities. If the flame zone is cooled, heat-producing reactions are slowed (proportional to T exp [-E/RT]); this may be carried to the point where insufficient heat is produced to maintain the flame reaction. Carbon dioxide, carbon tetrachloride, and methyl bromide undoubtly exert cooling as well as blanketing effects. By diluting the burning mixture without supplying heat itself, an extinguishing agent raises the heat capacity of the combustion system which, in turn, lowers the maximum temperature of the system. Inert gaseous nitrogen provides dilution and heat capacity effects, whereas liquid nitrogen can also provide cooling of the condensed fuel.

In practical situations, the problem of application can be the factor limiting the efficacy of the water in heat extraction. If the water does not reach the seat of the fire, it cannot help extinguish it. This is principally a question of the force and size dispersion of the jet. If the drops are too large, only a small fraction will evaporate and be effective. The remainder will run off. On the other hand, if the drops are too small, they will have poor carrying power, will not penetrate the fire region, and will also be wasted. The ordinary firefighting operation requires at least 10 times the minimal amount of agent, assuming perfect application. Thus, there is much room for improvement in sprays, nozzles, and other applicators.

Small fires can be blown out rather easily by an airstream of moderately high velocity. Here the gas-phase flame is fluid mechanically removed from the fuel. Basic mechanisms of flame stabilization are relevant directly to blowoff. All flames represent a balance between the flow of the combustible toward the flame zone and the flow of heat from the flame zone to the relatively cold combustible. It is possible to extinguish a flame by disturbing the flame zone. A disturbance of this sort can be effected by aerodynamic, magnetic, or electrical means. The blowing out of a match or the extinguishment of an oil fire by blasting are simple examples of aerodynamic means. Extinguishment with magnetic or electrical fields is more of a laboratory experiment than a practical measure, but it is a possible mode and explains the characteristics of a fire.

Another physical means of flame extinguishment is applicable to flame in which the transfer of radiant energy from the flame to the combustible is important. The interposition of an agent between the flame and (e.g., the unburned liquid) may result in reflection or absorption of enough radiant energy to result in flame extinguishment because of inadequate supply of the combustible to the flame zone.

Of the types of physical means indicated above, the blanketing or isolating effects and the radiation-blockage effect apply only to diffusion flames, not to premixed flames or monopropellant flames, where only one type of molecule is involved and enough heat is evolved in its decomposition to sustain flame. The cooling and mechanical effects have application to all types of flames.

Chemical Extinguishment

In addition to separating the fuel and oxidizer and cooling the condensed fuel and gas phase (i.e., slowing reaction by lowering the diffusion rate and the temperature of the reactants), it is also possible to inhibit reactions that occur in or before the flame front to extinguish the flame. Since the driving force of flames is a chemical reaction, it is apparent that interfering with critical reaction steps should suppress a fire. It is well-established that most preflame and flame reactions involve radicals and are chain reactions. Hydrocarbon burning involves the stripping of hydrogen atoms and the addition of oxygen atoms, and this burning is driven by reactive radicals. These radicals do not have a very high concentration but do affect a low activation energy reaction. An effective chemical extinguishant should serve to break the chain reaction.

The inhibition of chain reactions by small amounts of materials is well-known in chemistry, so the plausibility of chemical extinguishment by the breaking of chain reactions in the flame zone has good support. Because chemical extinguishment depends on the chemical reactivity of molecules in particular reactions, and because such reactivity can vary by orders of magnitude, the investigation of chemical extinguishment offers the most promise for the development of effective agents.

Halogen-containing compounds such as Halons 1301, 1211, and 2402 are the primary homogeneous chemical inhibitors for hydrocarbon fires. In general, chemical extinguishment has been achieved using volatile halides from the middle of the periodic table (e.g., carbon and phosphorus) and salts of the alkalic metals. The action of the former is in the gas phase, and the most popular explanation is that they exchange the reactive flame radicals (H, O, and OH) for relatively inert halogen atom radicals. The efficacy of a given family of these agents is inversely proportional to the reactivity of the atom (i.e., Br and I are most effective; F, the least). The low concentration required for fire suppression by the halons is a result of their chain-breaking action. The chemical reaction chain is broken by the halogen atom interacting with the driving radicals to slow heat production. Three mechanisms can be visualized: (1) the inhibitor reacts with a radical in the chain-branching step, reducing the burning rate; (2) the inhibitor may compete for a crucial radical in a nonbranching chain step; or (3) the inhibitor may increase the three-body recombination of radicals and by this means lower their concentration in the reaction zone. The first would be the most effective, but all of the mechanisms may be important under some conditions. Other views correlate extinguishing power with the electron attachment coefficient or the dipole moment, but the mechanisms associated with these correlations have not been as completely developed. The efficiency of the halons also stems from the recycling of the halogen atoms for reuse in their action with the usual flame radicals. Additionally, cooling is achieved via the latent heat of vaporization of liquid halons.

The applicability of the halons depends on the reactivity of the halogen atoms with the particular radicals, the reactions that are involved, and the temperature of the reaction. For example, when oxides of nitrogen are used as oxidizers, conventional inhibitors are ineffective. The flame of boron hydrides with oxygen is also atypical. Another point is the differences between flame inhibitors and detonation inhibitors. Halogenated compounds appear to promote detonation; iron pentacarbonyl inhibits both flames and detonations. This may be because halogenated inhibitors delay the flame reaction, forcing the initial reaction into a higher temperature range and increasing the local initial rate even though the overall rate (burning velocity) is decreased.

The principal heterogeneous chemical inhibitors are alkali metal salts, such as the dry chemical powders of sodium and potassium carbonates, sulfates and chlorides, and also ammonium phosphate. Whether the effective inhibiting reactions indeed are heterogeneous (occurring either on the surfaces of the original powder particles or on the surfaces of condensed particles such as oxides produced when the powder burns) or are, in reality, homogeneous (through chain-breaking by alkali metal hydroxides) has not yet been established. The chemical inhibitors often are used in conjunction with other extinguishants since often they either do not extinguish the flame completely nor do they allow it to reignite.

Powders appear to be heterogeneous in action. The most popular mechanism attributes extinction to the destruction of radicals by recombination on the particle surface. It has also been suggested that the action may be homogeneous due to volatilization of the particle, its dissociation, and possible radical recombination reactions of the flame radicals with the alkali metal. A third view, correlating ionization potential with efficacy, has not been systematically developed as a mechanism. Research has not been carried far enough to reveal the details of what happens when a powder is introduced into a flame. The dependence of effectiveness on surface area could be explained by assuming any of the following: (1) gaseous diffusion of flame species to the particles, followed by surface reactions which destroy chain carriers; (2) partial evaporation of the powder to form gaseous species which inhibit the combustion, the rate of evaporation being proportional to surface area; and (3) in cases where the flame is burning over a liquid, radiation from the flame to the fuel source is blocked to a degree dependent upon state of subdivision of the powder. The anion of alkali metal salts also has an effect. Easily decomposed salts such as carbonates and tartrates are especially effective. The most significant parameter for powder application is the surface area of the applied particles. The quantitative correlation between effective particle surface area and extinction capabilities suggests that a surface reaction is involved. One possibility is the three-body recombination of radicals on the surface. Two unexplained factors mar the simple picture. It has been pointed out that salts are only effective if they can be expected to volatilize or decompose during their residence in the flame. The effective reaction may be three-body recombinations of radicals involving the alkali metal formed by dissociation of the salt. The second disturbing factor is that a calculation of the upper limit for efficiency of such powders, assuming that every molecule which reached the particle surface recombines, indicates that both laboratory and field practice are more efficient than this theoretical upper limit. The calculation compared theoretical with minimum particle densities effective in quenching flames. The residence times available in the unperturbed flame front and estimated radical diffusion coefficients were used. This indicates that some vital factor has been omitted. Several possibilities exist. The particle may break up in the flame front due to boiling or decomposition so that the available surface area and particle count are greater than that measured for the particles applied. The residence time may be increased by the thermomechanical effect which can become comparable with flame velocities for small particles. The residence time for extinction may be longer than that estimated from the unperturbed flame, since as a flame is inhibited the burning velocity drops, increasing the residence time for the inhibition. Obviously a more sophisticated model must be used. Inhibition may occur in the gas phase, and the observed dependence on particle surface area may come about because the volatilization will depend directly on the surface area. More basic work is needed in this area.

There are a number of super-effective chemical suppressants, such as iron pentacarbonyl and lead tetraethyl, all of which almost certainly involve kinetic inhibition, since small amounts of these materials produce large effects. The chemical mechanisms by which they operate are not well understood and, in practice, they are often difficult to use because of toxicity problems. Often they do not produce complete extinction but lower the level of combustion so much that extinguishment by other agents is easy to achieve.

Most of the extinguishants and techniques have been developed for combustion of carbon and hydrogen compounds by oxygen. With a different flame chemistry, one would expect other extinguishants and techniques to be required. This is the case for reactive metal fires (which will be recognized when the results from using conventional extinguishants on fires of magnesium metal are presented later in this report). The firefighting technique often used for fires of reactive metals, such as magnesium and the alkali metals, has been to cover the burning metal with an inert blanket of fused salt, graphite, and so forth. Control,rather than extinction,is often the goal of such firefighting. These metals are used in large quantities in the Air Force and Navy; therefore, a need exists to develop a firefighting agent that can effectively extinguish a generally configured, three-dimensional metal fire.

Extinguishment of Burning Solids

References to magnesium fires and their inhibition are reviewed as extracted from ASTIA Document AD110685 (Reference 1). Delavault reports that silicon tetrafluoride, sulphur dioxide, and boron trifluoride inhibit magnesium combustion, while water accelerates it. Scartazzini used the optical pyrometer to measure flame temperatures of magnesium powder plus oxygen. Coffin developed a technique for determining burning times of magnesium ribbons in various atmospheres. He found that water accelerates the burning rate. He has not studied inhibitors with this technique. Tuve (Reference 2) stated that TMB, a viscous liquid (see Section III, Agents), is effective in extinguishing magnesium fires. McCutchan studied commercially available materials that might be effective in extinguishing a magnesium fire of the size and type to be expected in an aircraft crash. The effort was largely concentrated on liquids and nonaqueous foams. Materials were screened to determine their effectiveness on fires consisting of 5 pounds of magnesium scrap, the more effective agents being tested later on larger fires. Mixed fires of gasoline and aircraft-type scrap magnesium in quantities up to 400 pounds were successfully extinguished. Tricresyl phosphate or a solution of 9 to 7 percent orthoboric acid in triethylene glycol was effective. The resulting secondary fire can be controlled with either foam or water fog.

Greenstein and Richman (Reference 3) developed quantitative fire tests for evaluating extinguishing agents for magnesium fires, efficiency being measured in terms of the time of extinguishment, the quantity of agent required, and the quantity of unconsumed magnesium which remained at the conclusion of the test. By definition, a fire was said to be extinguished when the magnesium had been cooled to a temperature below its ignition point. Agents were studied both for cooling efficiency and for protection against reignition. The most successful agents consisted of solutions in bromochloromethane of liquids with high heat-absorbing capacity, such as 50 percent diisodecyl phthalate in bromochloromethane. The phthalate acts as the cooling agent, while bromochloromethane provides resistance to reignition by forming a protective film upon reaction with magnesium. The cooling efficiency of an agent of this type could be predicted quantitatively from the heat capacity and heat of vaporization of its components. Other means of enhancing reignition protection were also studied. The secondary fire was of limited intensity because of the presence of bromochloromethane and was extinguished on application of excess agent. In the absence of excess agent, the secondary fire was easily extinguished with bromochloromethane or with mechanical foam.

Approaches which are utilized in inhibiting oxidation have also been applied to actual fire extinguishing. The extinguishing action of boron compounds has been demonstrated with boron trichloride and boron trifluoride. These vapors, introduced into heat-treating and annealing furnaces, successfully extinguish magnesium fires. Although the action of the former depends, at least in part, on the formation of a protective film of magnesium chloride, the boron also plays a part.

The effect of a protective flux cover is simulated by a commercially available powder, which forms a fused salt film on the magnesium. A mixture of potassium acid sulphate, trisodium phosphate, bauxite, and pumice is also said to fuse around a magnesium mass at high temperatures, thereby, preventing contact with air.

Brown, Hartman, and Nagy (Reference 1) investigated solid materials which formed protective coatings. They found that hard pitch derived from coal tar was a more effective extinguishing agent than other substances, including salts and graphite. On contact with the hot metal, the pitch melts and forms a coating which excludes air.

Solid agents which stop combustion by mechanical protection from air accomplish little in cooling the magnesium to a temperature below its ignition point. The fusing agents absorb some heat in this process but, mostly, the protected mass is cooled by contact with the atmosphere. In the absence of rapid cooling, the coated mass can easily reignite if the protective layer is broken.

Graphite is probably an exception among the powdered extinguishing agents. Thrune (Reference 1) recommended the use of tri(p-tert-butylphenyl) phosphate or other aromatic triesters of phosphoric acid in an excess of finely divided graphite. The phosphate absorbs heat in vaporizing and simultaneously forms a vapor blanket which excludes air. The bulk of the cooling is accomplished by the high thermal conductivity of the graphite.

In a second approach to the firefighting problem, the major consideration is cooling, which is most effectively brought about by the use of liquids. Those which have been proposed have generally had high flash points, but nevertheless burned on contact with the magnesium fire. A patent by Farris et al. (Reference 1) offers mixtures of vegetable oils as extinguishing agents, the oil being applied as a foam containing an inert gas, such as nitrogen or carbon dioxide, to control the secondary fire. Friedrich (Reference 1) suggested a foam consisting of paraffin oil and carbon dioxide.

Another patented liquid extinguishing agent consists of mineral oil and a chlorinated hydrocarbon; the latter component is said to extinguish the secondary fire. Factory Mutual Research Corporation investigated mixtures of high flash point motor oil or tricresyl phosphate with methyl bromide, with only moderate success.

Models of Burning Magnesium

The physics of diffusion flame models and the homogeneous chemical reaction mechanisms for the burning of magnesium are reviewed below as extracted from a thesis by R. F. Whitacre (Reference 4). First some fundamental hypotheses, which are based on basic applications of the thermodynamic behavior of metals and their oxides, are presented.

Thermodynamic Fundamentals of Burning Metal

The upper limit of the flame temperature is a value equal to the boiling point of the metal oxide. This hypothesis is based upon the facts that (1) for most metals, the heat of vaporization or dissociation of their oxides is greater than the exothermic heat of formation of the oxide; and (2) many of the oxides tend to dissociate upon vaporization, hence offering a further energy barrier at the boiling point of the oxide. A consequence of the upper limit on the flame temperature is an equilibrium of the condensed oxide with its vapor-phase decomposition products.

If the boiling point of the metal oxide is greater than the boiling point of the metal, then steady-state combustion takes place in the vapor phase. For the opposite case in which the boiling point of the metal exceeds the boiling point of the metal oxide, a surface combustion process is expected. This hypothesis can be justified by examining the criterion for the idealized hydrocarbon droplet burning model. If vapor-phase burning is to occur, then the maximum temperature (flame temperature) must be at some finite distance from the surface of the droplet so that the energy for vaporization of the fuel is transferred from the reaction zone to the surface of the fuel. Since the temperature will be limited to the boiling point of the metal, the criterion for vapor-phase burning is that the flame temperature is greater than the boiling point temperature of the metal. For the condition of vapor-phase burning, from the first hypothesis in the preceding paragraph, the flame temperature is limited to the boiling point of the metal. Thus, the boiling point temperature of the metal oxide is greater than the boiling point temperature for vapor-phase combustion. This hypothesis is necessary but not a sufficient condition for vapor-phase combustion because the heat losses could lower the flame temperature below the boiling point of the oxide.

In metal combustion, radiation to the fuel surface and to the surroundings is an important hypothesis because of the high temperatures present in a metal flame and the presence of condensed-phase oxide particles.

The ignition phenomena to begin a metal fire could be entirely different from the controlling steady-state combustion phenomena. This hypothesis allows for preignition reactions, which are generally surface reactions, while steady-state combustion could occur by a vapor-phase mechanism. There is no reason to expect that the same mechanism should occur for both cases. The fact that condensed phase particles exist in metal combustion furthers the importance of heterogeneous reaction processes. Unless the metal and oxidizer are premixed, the ignition of the metal is always preceded by reactions on the surface or within a protective oxide layer. Upon ignition, the reaction will continue to occur within the molten oxide layer. The combustion process may also occur in the vapor phase. The vapor-phase reaction mode will exhibit a high burning rate, a luminous region between the metal and the outer region, and the presence of oxide smoke particles with a submicron characteristic size. Thus, it would appear that for metals which burn in the vapor phase, the transport processes will dictate the reaction rates. Upon ignition, fuel particles burn in a self-sustaining, vapor-phase reaction.

Diffusion Flame Models. Various models have been proposed to represent the flame structure of metal-oxygen diffusion flames. Most of these models are similar to the ideal hydrocarbon droplet flame model. The critical determination of the correctness of a model is not possible because many of the theromodynamic and transport parameters needed for analytical calculations of the burning rate are not known or are uncertain. These uncertainties in properties of polyatomic mixtures make the evaluation of the flame structure models impossible for aluminum because all the idealized and simplified models are in agreement with existing experimental data.

Finite Reaction Zone Model by Coffin. The earliest model of a diffusion flame is due to Coffin (Reference 1). Coffin investigated the burning of magnesium ribbons in various oxygen-diluent mixtures. It was noted that the vapor-phase reaction of magnesium is analogous to the combustion of a liquid fuel droplet. But instead of a collapsed flame front as exists in the combustion model of a liquid fuel droplet, Coffin defined a reaction zone of a finite thickness. The model contains three concentric zones. The inner zone contains only the pure metal in the vapor phase and the inert diluent. Metal from the fuel surface is vaporized by heat conducted back to the metal surface from the reaction zone. This evaporated metal diffuses to the reaction zone, assumed to be at the boiling point of the oxide. This is a statement of the first hypothesis. This temperature is in agreement with previous investigations. Most of the oxide was believed to be at the boiling point and hence tended to dissociate, thereby offering another energy barrier for further increase in the flame temperature. The reaction zone consists of a mixture of metal vapor, oxygen, and condensed oxide at the boiling point of the metal oxide. Chemical equilibrium was assumed throughout the reaction zone.

The outermost zone consists of oxygen diffusing toward the reaction zone and condensed metal oxide traveling outward. The oxide cools and exchanges energy with the inward diffusing oxygen so that the temperature of the oxygen is at, or near, the flame temperature when it enters the reaction zone. The model is intrinsically assumed to be a steady-state representation, and free convection was ignored.

Liquid Oxide Bubble Model by Fassell. Fassell et al. (Reference 1) presented evidence that while the gas-phase spherical diffusion flame theory adequately accounted for the burning of magnesium, for metals with higher boiling points, the model suggested by Coffin did not lead to a satisfactory explanation. In their experiments, Fassell et al. burned aluminum and various aluminum-magnesium alloy particles in two different types of torches (methane-oxygen mixtures, or a combination of methane, oxygen, and air).

When Fassell et al. found numerous hollow oxide spheres in the combustion products, they molded the observed processes as a continuous layer of molten oxide covering the metal droplet. The metal evaporating from the droplet, which is assumed to be at its boiling point, causes the oxide layer to form a bubble. Hence, the oxide layer limits further combustion. The diffusion of the metal outward through the molten oxide layer and the diffusion of the oxygen inward are the limiting steps. The reaction is considered to take place at the liquid oxide inner surface. The authors also considered the possibility of the bubble exceeding a critical diameter and fragmenting, thereby resulting in a scatter of both oxide and pure metal fragments.

Collapsed Reaction Zone Model by Brzustowski and Glassman. The model due to Coffin subsequently came under criticism by Brzustowski and Glassman (Reference 1). They felt that radiation from the flame front to the surface and surroundings should be considered, that the diffusion of oxygen from the surroundings should be affected by the presence of the condensed oxide combustion product, and that the thick reaction zone used by Coffin predicted a flame structure "notably different" from observed flames.

The analysis by Brzustowski and Glassman was based on the theory developed to describe the combustion of hydrocarbon droplets, but was modified to account for specific characteristics peculiar to metal combustion. These features are as follows:

a. The flame temperature will be fixed at the boiling point of the oxide. Some oxide will always form in the condensed state.

b. The presence of the condensed oxide products will affect the diffusion of oxygen to the reaction zone. Movement of these solid or liquid products must occur due to bulk motion of gaseous species since they cannot diffuse.

c. Thermal radiation will probably be an important consideration because of the existence of these condensed species in the high temperature regions of the flame. It can possibly result in higher evaporation rates for the fuel due to an increased heat feedback, but it can also lead to significant losses to the surroundings.

d. In the case of metal combustion, evaporation rates of the fuel may not be fast compared to diffusional processes.

With these considerations, the collapsed flame zone model was proposed. The metal fuel at the surface is evaporated by the conduction and radiation modes of heat transfer from the thin flame front. This metal, which may be several hundred degrees below the metal oxide boiling point, diffuses toward the flame through a stagnant film. The oxidizer diffuses inward toward the flame front. The oxidizer diffusion is inhibited by the outward movement of the combustion products which were formed at the flame front. The idealizations in this model are a steady-state system in time and no back-diffusion of combustion products.

Brzustowski found Coffin's distributed reaction zone model unacceptable primarily because it assumed no gaseous oxide was present due to complete dissociation, whereas spectroscopic observations showed significant oxide vapor radiation. Also, Brzustowski felt his flame photographs defined a different model. Over a large pressure range (50 torr to 12 atm), Brzustowski thought that the bright flame zone thickness was small, compared to the distance between the metal surface and the flame front.

Extensions of the Brzustowski-Glassman Model by Christensen. Christensen, Knipe, and Gordon (Reference 1) undertook a survey on aluminum particle combustion and discussed the available models, as well as the Brzustowski-Glassman models. The group criticized the Fassell model, since it purported that the limiting step is the diffusion through the oxide layer, and that the magnitude of this diffusion rate is uncertain. The model does consider the normal metal oxide coating which exists on the metal particles prior to ignition, but the bubble proposed by Fassell may be unstable.

The Brzustowski-Glassman model is criticized since it does not consider the presence of a metal oxide layer prior to ignition. Christensen et al. concluded that the Brzustowski-Glassman model does describe the gross features of aluminum particle combustion, but that some important features are not included in the model. On the basis of this conclusion, Christensen et al. sought to extend the Brzustowski-Glassman model to incorporate the most significant features not included in the model.

In the Brzustowski-Glassman model, back-diffusion of the combustion products was assumed not to take place. However, experimental observations at the Naval Ordnance Test Station (NOTS) showed that significant amounts of oxide did build up on the metal surface during combustion, indicating that more than just the metal and the inert diluent are present in the inner zone. On the basis of back-diffusion, oxygen-containing species (both evaporation products and partially reacted species) make up a saturated vapor relative to condensation. A second nucleation zone is proposed on the oxidizer side of the reaction zone.

Heterogeneous Reaction Model by Markstein. While Markstein (Reference 1) did not actually specify a model, his work with vapor-phase burning has contributed significantly to the problem of whether or not homogeneous reaction or heterogeneous reaction dominates metal combustion, particularly with magnesium. He presented most of the processes which could play an important part in the vapor-phase combustion. Markstein states that heterogeneous reaction on the metal surface is not significant once the vapor-phase diffusion flame is fully developed. Back-diffusion of oxide vapor is expected to be significant as evidenced in the experimental work by Macek (Reference 1).

In an earlier work, Markstein pointed out the strong role of heterogeneous reaction in low pressure dilute magnesium-oxygen flames.

A typical model employing the proposals of Markstein would involve nucleation regions which are not well-defined as they are in the Knipe model. Markstein stated that initially some homogeneous reaction may occur to furnish sites for the ensuing heterogeneous reaction, but that once the flame is fully developed, the heterogeneous mechanism would become dominant. Due to the dominance of the heterogeneous reaction, vapor-phase oxide is not present in significant quantities, and hence back-diffusion is neglected.

The Inner Reaction Zone Model by Sullivan. Sullivan undertook an experimental investigation to determine the flame structure of metal vapor-phase diffusion flames of the alkaline-earth metals Mg, Ca, and Sr.

This investigation has shown that reaction does occur in the inner zone of the luminous envelope surrounding the metal sample. The homogeneous reaction initially leads to a supersaturation of oxide vapor which, in turn, leads to rapid nucleation. Thus, the inner zone is expected to be a high-temperature region of the flame due to the liberation of the heat of condensation. Sullivan demonstrated that the major contribution to the observed radiation is caused by a thermal excitation mechanism, although some contribution from chemiluminescent radiation may occur in the inner reaction zone.

The flame zone is not a collapsed flame zone as in the model of Brzustowski and Glassman. The maximum flame temperature is not expected to be located at the outer edge of the luminous envelope. The reaction zone appears to extend to regions very close to the wire surface.

Sullivan defines a flame structure model in which a predominantly homogeneous reaction zone is located well within the luminous envelope. The condensation of the oxide vapor accounts for the excitation of the species observed to radiate. The outer limits edge is thought to occur due to the pileup of oxide particles. The pileup occurs due to a decrease in bulk velocity of products and thermophoresis effects as the particles move away from the reaction zone.

Homogeneous Kinetics of Magnesium Oxidation

A summary of the thermophysical models, which was presented in the preceding section, is presented below so that the succeeding review of the homogeneous reaction kinetics for the oxidation of magnesium is viewed in the state-of-the-art perspective (Reference 1).

It is first noted that the only combustion product from burning magnesium in air is magnesium oxide which is solid up to 2800°C. Magnesium itself melts at 651°C and boils at 1110°C. Hence, similarities of magnesium combustion with carbon combustion should not be expected. Additionally, magnesium can react in a pure nitrogen environment.

Physical and chemical methods of fire suppression are considered for the origination/development of an extinguishant for magnesium fires in air. Therefore, knowledge of the reaction mechanism(s) will assist in the formulation and performance evaluation of such an extinguishant.

Summary of the Thermophysical Models

The original research accomplished by Coffin typifies the fundamentals of the thermophysical models. Coffin studied the rate at which magnesium ribbons burn in various atmospheres of oxygen plus inert gas. He believes that the magnesium boils and undergoes vapor-phase combustion. He assumes the reaction-zone temperature to be governed by the boiling point of magnesium oxide (about 3000°C) and the magnesium oxide is considered to dissociate upon vaporization. The result is a chemical equilibrium between condensed oxides, magnesium vapor, and oxygen, in a stagnant film of inert gas. For this model, the burning rate may be calculated from the observed flame diameter, the diffusion coefficient of the oxygen, and the thermal conductivity of the gas between the flame and the surface. Such calculations obtained burning rates in reasonable agreement with experiment. This constitutes a strong argument that chemical rate constants play no role in determining the burning rate of magnesium. However, Coffin did some experiments which showed that the addition of a small amount of water vapor to oxygen-argon mixtures substantially increased the burning time from 4.2 to 5.7 seconds. Because this type of behavior suggests that the rate of the process cannot be governed entirely by physical effects. Further studies are needed. To summarize the situation with regard to magnesium fires, it seems possible to explain the rate of burning of magnesium and the action of the known extinguishing agents purely on a physical basis (with the exception of Coffin's lone observation of the accelerating effect of moisture), but there is no real proof that chemical inhibition may not be possible.

Summary of Reaction Mechanisms

Primarily, four mechanisms found in the literature were considered for the oxidation of magnesium:

(1) Heterogeneous mechanism.

(2) Dimer mechanism.

(3) Third-body mechanism.

(4) Peroxide mechanism.

These four mechanisms were originally postulated to explain the observations of calcium flames.

Heterogeneous Mechanism. The elementary steps for the heterogeneous mechanism are

	$\Delta H_{\text{reaction, 298K}}^{\text{kcal}}$
(1) $2Mg(s) \rightarrow 2Mg$	70.6
(2) $Mg + O_2 \rightarrow MgO + O$	25.3
(3) $MgO \rightarrow MgO(s)$	-144.7
(4) $Mg + O \rightarrow MgO(s)$	-238.6

and the overall reaction is

$2Mg(s) + O_2 \rightarrow 2MgO(s)$	-238.6

Since the vapor-phase formation of Reaction (2) is endothermic, it will not excite MgO to the energy levels responsible for the emission in the flame, the lowest of which requires 57 kcal/mole. Therefore, the total observed radiation of the flame should be representative of the thermal excitation and equilibrium at the boiling point of the oxide, which was previously shown to be the maximum flame temperature. Chemiluminescence will not provide an appreciable part of the observed radiation. The two primary criticisms of this mechanism are that chemiluminescence is not predicted, and the homogeneous condensation rate of the oxide within the flame may not be consistent with the reaction rates.

Dimer Mechanism. Since the phenomenon of chemiluminescence has been observed in the radiation of metal flames, it is apparent that the mechanism must include a vapor-phase, exothermic reaction of sufficient energy to cause chemiexcitation of Mg or MgO to the energy levels observed. The dimer mechanism satisfies this condition. The elementary steps for the dimer mechanism are

	$\Delta H_{\text{reaction, 298K}}{}^{\text{kcal}}$
(5) $2Mg(s) \rightarrow Mg_2$	60.0
(6) $Mg_2 + M \rightleftarrows 2Mg + M$	0.0
(2) $Mg + O_2 \rightarrow MgO + O$	25.3
(7) $Mg_2 + O \rightarrow MgO + Mg$	-83.3
(8) $2MgO \rightarrow 2MgO(s)$	-289.4

and the overall reaction is

$$2Mg(s) + O_2 \rightarrow 2MgO(s) \qquad -287.4$$

For the dimer mechanism, reaction (7) is sufficiently exothermic to result in the observed chemical excitation of MgO and Mg. The magnesium dimer, which is known to exist, does not have a very large equilibrium concentration. A plot of the theoretical and experimental dimer mole fraction versus temperature shows just how small the mole fractions are.

A comparison of the data for such a plot is presented in Table 1.

TABLE 1. MAGNESIUM DIMER MOLE FRACTION VERSUS TEMPERATURE.

	$k_p \times 10^3$		$x_{Mg_2} \times 10^3$	
T(k)	Calculation	Experimental	Calculation	Experimental
600	9.81	6.502	9.622	6.419
800	3.94	3.990	3.909	3.958
1000	2.07	2.644	2.062	2.630

The theoretical work also shows reasonable comparisons between the calculated heat of sublimation or vaporization of Mg_2 of 59.2 ± 4.4 kcal/mole, and the experimental value of 63.4 ± 0.7 kcal/mole; and between the calculated bond energy at 1100 K of -6.2 kcal for the Mg_2 molecule, and the spectroscopic dissociation energy of 6.92 kcal/mole. The good comparison between these values justifies the validity of the Stogryn and Hirschfelder equations for estimating the bond energies.

Third-Body Mechanism. A second chemiluminescent mechanism is referred to as the third-body reaction [Reaction (9) below]:

		$\Delta H_{reaction,\ 298K}$ kcal
(1)	$2Mg(s) \rightarrow 2Mg$	70.6
(2)	$Mg + O_2 \rightarrow MgO + O$	25.3
(9)	$Mg + O + M \rightarrow MgO + M$	-93.9
(8)	$2MgO \rightarrow MgO(s)$	-289.4

and the overall reaction is

$$2Mg(s) + O_2 \rightarrow 2MgO(s) \qquad -287.4$$

For this mechanism, note that reaction (9) is sufficiently exothermic to result in observed chemical excitation of Mg and MgO.

A third mechanism has been proposed by Gordon et al. (1968), which postulates the presence of a peroxide of Mg, namely MgO_2:

		$\Delta H_{reaction,\ 290K}{}^{kcal}$
(1)	$2Mg(s) \rightarrow 2Mg$	70.6
(11)	$Mg + O_2 \rightarrow MgO_2$	?
(12)	$MgO_2 + Mg \rightarrow 2MgO$	?
(4)	$2MgO \rightarrow 2MgO(s)$	-289.4

and the overall reaction is

$$2Mg(s) + O_2 \rightarrow 2MgO(s) \qquad -287.4$$

The peroxide formed by Reaction (11) is not a stable species, but a reaction intermediate, i.e., longer lived than a normal complex. For this mechanism, it is also assumed that Reaction (12) is sufficiently exothermic to cause chemiluminescence.

Summarizing the mechanisms, it is felt that the third-body mechanism is the most likely mechanism. An investigation of the magnitudes of the equilibrium constants in Table 1 shows that the reaction

$$Mg_2 + O \rightarrow MgO + M$$

should not be competitive with the reaction

$$Mg + O + M \rightarrow MgO + M$$

unless the pressure is very low. At a low pressure, the ratio of two-body to three-body collisions overshadows the differences in concentrations. According to the literature, this will occur at pressures less than 10^{-3} atmospheres.

Because the homogeneous chain propagating reaction

$$Mg + O_2 \rightarrow MgO + O$$

is endothermic (+25.3 kcal/mole), it is felt that a termolecular reaction with a low activation energy may be competitive with a bimolecular reaction like the one above.

The peroxide mechanism is based on the postulated existence of an intermediate which has not been observed; hence, the mechanism which seems the most likely is the third-body mechanism.

Note that in all the mechanisms presented above, the heterogeneous reaction may be present in the overall mechanism. According to the literature, the process of nucleation is the slowest phase of the heterogeneous reaction involving three phases (nucleation, growth, and agglomeration); hence, the heterogeneous reaction may be the rate-controlling step in the mechanism. The heterogeneous reaction appears to be a function of temperature. As the temperature increases, the importance of heterogeneous reactions seems to decrease. This is an extension of the results of a study which examined heterogeneous reactions at temperatures well below the flame temperatures characteristic of Mg combustion.

Looking at a basic model for the metal diffusion flame, it has been shown that the inner zone is a region of reaction. There is almost certainly a deviation from equilibrium conditions. It is expected that some of the nonequilibrium radiation is due to chemiluminescence.

EXISTING EXTINGUISHING AGENTS FOR METAL FIRES

A search of manufacturers, suppliers, researchers, and literature was made to determine the currently existing firefighting agents appropriate to burning aircraft metals. Table 2 lists the solid, liquid, and gaseous extinguishing agents identified in this search. Appendix A contains a bibliography of the literature examined during this search.

A search of computer indices for material pertaining to magnesium and aircraft metal fires and extinguishing agents published since 1960 indicated that most of the research in recent years has been directed toward fires in sodium, sodium-potassium alloys, lithium, uranium, and plutonium. These are metal fire hazards primarily associated with nuclear industry and research. Much of the literature referenced in the material published between 1960 and the present refers to the 1940s and 1950s. G-1 powder, one of the few approved agents, was described in a 1944 publication. The patent for one of the most widely used current Class D agents, namely MET-L-X, was issued in 1960. As these dates indicate, not many new extinguishing agents for fires in magnesium and other light metals have been identified in the last 20 years. No agents were identified that satisfied the general configuration capabilities desired, including both vertical and indirectly accessible fires.

TABLE 2. METAL FIRE-EXTINGUISHING AGENTS.

Solids

1. G-1 powder
2. MET-L-X powder
3. Na-X powder
4. Foundry flux
5. Lith-X powder
6. Pyromet powder
7. T.E.C. powder
8. Talc powder
9. Graphite powder
10. Sand
11. Cast iron borings
12. Sodium chloride
13. Soda ash
14. Dolomite
15. Carbon microspheres
16. X-8 powder
17. Glass fritz
18. Polyvinyl chloride and sodium borate
19. Perlite
20. Vermiculite
21. Calcium fluoride
22. Lithium fluoride
23. Lithium chloride
24. Lithium hydroxide
25. Asbestos
26. Feldspar
27. Amonium chloride
28. Borax
29. Boric oxide
30. Pitch

Liquids

1. TMB liquid
2. M-X liquid
3. Water
4. Liquid nitrogen
5. Carbon tetrachloride
6. Parafin - CO_2 foam
7. Inorganic esters of H_3PO_4, SO_2, and H_3BO_3
8. Casein, talc, and $MgCO_3$
9. Liquid halocarbons
10. H_3BO_3 - glycol mixture
11. Halophosphates
12. Tricresylphosphates
13. Silicon oil
14. JP-4
15. Heavy mineral oil
16. Bromochloromethane and di-isodecyl phthalate

Gases

1. Boron trifluoride
2. Boron trichloride
3. Nitrogen gas
4. Argon

The composition and characteristics of the agents identified are presented in the following paragraphs.

G-1 Powder (Metalguard Powder)

This powder is UL-listed for magnesium and magnesium alloys and Factory Mutual System-approved for use on fires in magnesium, aluminum, sodium, potassium, and sodium-potassium alloys. It consists of screened graphitized foundry coke to which an organic phosphate has been added. The graphite absorbs heat and conducts heat away from the fire, reducing the metal temperature below the ignition point. The graphite particles form a closely packed blanket, partially smothering the fire, while the organic material breaks down with heat, producing a smoky gas that fills the voids between graphite particles, further excluding air from the fire. The powder is nontoxic and noncombustible. The packing characteristic of the powder prevents its discharge from a fire extinguisher.

MET-L-X Powder

This powder is UL-listed for use on fires in magnesium, sodium, potassium, and sodium-potassium alloys. It consists of a sodium chloride (86 percent) base with additives including tricalcium phosphate (1 percent) to improve flow characteristics, metal stearates (1 percent) for water repellency, and a thermoplastic material (7 percent) to bind the sodium chloride particles together when applied to the fire. MET-L-X forms an oxygen-excluding barrier as the sodium chloride melts and flows together. The thermoplastic binding allows this barrier to adhere to vertical surfaces. MET-L-X is noncombustible, nonabrasive, and nonconductive. It is discharged from 13.61- to 158.76-kilogram (30- to 350-pound) extinguishers and up to 907.2-kilogram (2000-pound) piped systems propelled by CO_2 or nitrogen. This is one of the few agents which claimed to be capable of fighting fires on vertical surfaces.

Na-X Powder

This powder is UL-listed for fires involving sodium metal. It is a sodium carbonate-based agent with additives to render the agent nonhygroscopic and easily fluidized for discharge from extinguishers. Na-X forms a crust over the burning metal, excluding air. It does not adhere to vertical surfaces and is not especially effective on magnesium fires.

Foundry Flux

Numerous fluxes are available for use in magnesium foundry operations. Consisting of various amounts of potassium chloride, barium chloride, magnesium chloride, sodium chloride, and calcium fluoride, they form either a molten or crust barrier between molten metal and air. Stored in covered steel drums and applied by hand scoop or shovel, a relatively small amount of flux, carefully applied, will exclude air from a large surface of burning metal.

Pyromet Powder

Pyromet consists of sodium chloride, diammonium phosphate, protein, and a waterproofing and flow-promoting agent. It has proven effective in handling fires involving sodium, calcium, zirconium, titanium, magnesium, and aluminum in powder and chip form. The fire is extinguished by burying with the powder.

T. E. C. Powder

Ternary eutectic chloride (T.E.C.) powder consists of barium chloride (51 percent), potassium chloride (29 percent), and sodium chloride (20 percent). It acts in a manner similar to foundry flux. T.E.C. powder was found to be most effective on sodium, potassium, and sodium-potassium alloy fires but was also reported to be effective against magnesium chip fires and small uranium and plutonium fires in scientific glove boxes. Barium chloride is toxic.

Talc Powder

Talc is composed primarily of silicon dioxide and magnesium oxide. It acts as an insulation to control rather than extinguish the metal fire. In a magnesium fire, the silicone dioxide breaks down to provide oxygen to the fire.

Graphite Powder

The action of graphite powder is similar to that of G-1 powder, absorbing and conducting heat away from the fire, but without the sealing effect of the organic smoke. Extinguishment is not as rapid as with G-1 powder.

Sand

Dry sand has often been recommended for controlling and extinguishing metal fires. The fire must be completely buried. Even after a fire is completely buried, the fire can obtain oxygen from the silicon dioxide in the sand and will continue to burn. Moisture in sand can react violently with the burning metal.

Cast Iron Borings

Cast iron borings have been used in machine shops to extinguish small metal chip fires. The iron acts as a coolant, extinguishing the fire. Oxidized or moist borings must be avoided.

Sodium Chloride

Sodium chloride acts to extinguish magnesium and alkali metal fires by forming a sealed coating on the metal surface, excluding oxygen.

Soda Ash

Soda ash is primarily sodium carbonate. It acts similarly to sodium chloride. It is recommended for use on sodium and potassium fires.

Dolomite

Dolomite is composed of calcium carbonate and magnesium carbonate. It acts by smothering the fire. The fire must be completely buried. It has been used on magnesium, sodium, zirconium, and titanium fires. It was shown to be less effective than T.E.C. powder on magnesium fires.

Carbon Microspheres

Fluidized petroleum coke microspheroids of 100-300 μm in diameter are the recommended form. Carbon microspheres act to cool and smother the metal fire. Tests have reportedly shown effectiveness on sodium, potassium, lithium, sodium-potassium alloy, and magnesium fires. This agent can be applied by pressurized extinguishers and is noncorrosive.

X-8 Powder

X-8 is a granulated shale-like material mixed with a form of pitch and crystalline ammonium chloride. Applied by shovel to cover the burning metal, X-8 can be used on almost all of the combustible metals. It is nontoxic and noncombustible.

Glass Frits

Glass frits consisting of SiO_2 (41 percent), Al_2O_3 (17 percent), K_2O (3 percent), Na_2O (7 percent), B_2O_3 (30 percent) or ZnO (16 percent), SiO_2 (41 percent), CaO (4 percent), Na_2O (9 percent), and B_2O_3 (30 percent) have been shown to be effective in controlling magnesium fires and containing shallow molten magnesium flows. These frits with melting ranges of 750-850°C fuse when applied to a magnesium fire, providing a glass barrier which is self-healing between the metal and air. However, in small-scale tests, magnesium contained under the glass surface continued to burn, probably extracting oxygen from the oxides in the glass. Glass frits are noncorrosive, nonhygroscopic, and can be dispensed from pressurized extinguishers.

Polyvinyl Chloride and Sodium Borate

A one-to-one mixture of these two chemicals and 1 or 2 percent flow additives produce a powder which forms an oxygen-restricting coating on the metal surface which enables a fine water spray to be used to cool the fire to extinction. The powder is inexpensive to produce and does not cake or clog discharge nozzles. Small amounts of acid vapor are given off upon application to the fire.

Perlite

Consisting primarily of silicone oxide and aluminum oxide, perlite has been used to effectively smother magnesium fires.

Vermiculite

Consisting primarily of silicone oxide, aluminum oxide, and magnesium oxide, vermiculite is less effective than perlite in extinguishing magnesium fires.

Calcium Fluoride

Calcium fluoride has been tested on fires involving sodium, potassium, lithium, magnesium, titanium, and uranium with mixed results. It was shown to be the most effective agent for titanium turbine blade fires with only mediocre results on magnesium fires. Extinction is effected by heat absorption and oxygen exclusion.

Other Solids

Lithium fluoride, lithium chloride, lithium hydroxide, ammonium chloride, boric oxide, borax, asbestos, feldspar, powdered pitch, and powdered soapstone have been mentioned as extinguishing agents for various metals with limited effectiveness.

TMB Liquid

TMB liquid agent contains an excess of methanol to render it free-flowing. The agent is applied as a spray or straight stream. A heat flash is produced on contact with the metal fire due to the breakdown of the compound and ignition of the methanol. A molten boric oxide coating formed on the hot metal prevents contact with air. TMB has been used on fires in magnesium, zirconium, titanium, and small amounts of sodium. The agent will hydrolyze readily, forming boric acid and methanol. The boric oxide smoke produced during fire extinction is toxic.

M-X Liquid

This liquid petroleum derivative is specifically recommended for magnesium chip fires. The liquid cools and smothers the fire. Secondary Class B fires may develop, but irritating fumes and smoke are not given off. M-X liquid is nonconductive, nontoxic, nonabrasive, and noncorrosive.

Water

Although water in small quantities accelerates magnesium fires, rapid application of large quantities of water is effective in extinguishing magnesium fires. Extreme caution must be exercised in fighting magnesium fire with water. Water is not recommended in fighting any other metal fires except zirconium and titanium by immersion. Extinguishment is generally accomplished by cooling. Metal fires will decompose to hydrogen and oxygen, providing oxygen to the metal fire and the potential for a hydrogen explosion.

Liquid Nitrogen

Extinguishment of metal fires using liquid nitrogen to cool and exclude oxygen from the fires is discussed, in the literature. A closed environment is required for the system discussed, and extinguishment is very slow in occurring. In this system, liquid nitrogen is not applied to the metal; it is vaporized in the atmosphere surrounding the fire.

Other Liquids

Carbon tetrachloride; paraffin-CO_2 foam; inorganic esters of H_3PO_4, SiO_2, and H_3BO_3; casein, talc, and $MgCO_3$; liquid halocarbons; H_3BO_3-glycol mixture; NaCl and $MgCO_3$ mixtures; halophosphates; tricresylphosphates; silicon oil; TP-4; and heavy mineral oil are mentioned in one or more literature sources as liquid extinguishing agents of limited effectiveness.

Boron Trifluoride and Boron Trichloride

Both of these gases are used in heat-treating furnaces to control magnesium fires. The gas excludes air from the fire and its presence must be maintained until the metal is cooled below the ignition temperature or the metal will reignite upon contact with air. The fluoride is more effective than the chloride; both are extremely toxic.

Nitrogen

Nitrogen gas used to exclude oxygen from metal fires is not very effective without the cooling effect of vaporizing liquid nitrogen. Even with the cooling effect, extinguishment and temperature reduction are slow and are only practicable in confined spaces.

Argon

Argon has been effective under certain conditions in controlling or extinguishing zirconium, lithium, sodium, potassium, and titanium fires. An argon gas blanket excludes air from the metal surface.

AGENT PERFORMANCE TESTS

Performance tests were conducted on the agents listed in Table 3. Agents were first tested on small piles of magnesium turnings under a laboratory hood to observe reactiveness and effectiveness of the agent. Agents which proved effective in these small-scale tests and other agents of interest were then tested in a larger, medium-scale vertical and indirectly accessible fire. Some agents tested in the small scale reacted so violently that they were excluded from the larger-scale tests. In addition to the agents identified as potential metal fire-extinguishing agents, general purpose agents used by the Air Force, including water, AFFF, dry chemical, and Halon 1211, were tested and their reactions observed. All testing was documented on video recordings.

Small-Scale Tests

In the small-scale tests, 40 ml (approximately 16.5 grams) of coarse magnesium turnings were placed in a pile on an asbestos board under a laboratory hood. The turnings were ignited using a propane torch and were allowed to burn until better than two-thirds of the surface of the pile was involved. Agents were then applied in small quantities at small rates. The quantity and rate of agent application were then increased until the metal fire was controlled, if possible. Solid agents were sprinkled from small scoops, and liquids were applied from spray bottles or poured from open vessels. The reactions that occurred when the agents were applied, the effectiveness of the agents at extinguishing the fire, and evidence of the agents adhering to vertical surfaces or extinguishing indirectly accessible portions of the fire were noted.

Medium-Scale Tests

Medium-scale testing was carried out in specially developed apparatus which repeatedly produced horizontal, vertical, and indirectly accessible

TABLE 3. EXTINGUISHING AGENTS TESTED IN PHASE I.

Agent	Scale tested
MET-L-X	S, M
Graphite powder	S
Sodium chloride	S
Dry chemical (sodium bicarbonate)	S, M
Dry chemical (potassium bicarbonate, PKP)	S, M
Dry chemical (ammonium phosphate)	S
Talc powder	S
Sand (dry)	S
Glass (powder)	S
Glass (flakes)	S
Glass (spheres)	S
TMB liquid	S, M
Water	S, M
AFFF (aqueous film-forming foam)	M
Halon 1211	S
Halon 2402	S
N_2 (liquid)	S, M
Silicon grease	S
N_2 (gas)	M
CO_2	M

metal fires. Because the melting temperature and ignition temperature for magnesium are so close and because magnesium is such a good conductor of heat, it is difficult to initiate and sustain a magnesium fire in the vertical orientation. The entire test sample tends to soften and flow about the same time the sample ignites, resulting in a horizontal magnesium fire wherever the magnesium stops flowing. The apparatus shown in Figure 1 was developed by NMERI to produce metal fires in the vertical and indirectly accessible configurations. The apparatus consists of a shallow crucible suspended approximately 1.524 meters (5 feet) above ground level, a screen running from the crucible spout to a ground anchor point at an angle near vertical, a heat shield with an opening for observation and agent application which limits the agent accessibility to the fire, and propane torches for heating and igniting the metal sample. As the metal sample in the crucible was heated, the outer surface of the sample would ignite and melt. When the molten metal filled the crucible, it would flow onto and down the screen. Some of the metal adhered to the screen, and the rest accumulated behind the screen at ground level. The fully established fire produced by this apparatus consisted of a partially melted burning ingot in a burning molten pool of metal feeding a flowing, burning vertical sheet of molten metal approximately 1.22 meters (4 feet) long by 101.6 millimeters (4 inches) wide feeding a burning molten pool of metal at ground level behind the screen. Two types of vertical configuration fires are present in this fire. The short vertical surfaces of the burning ingot are relatively stationary, while the vertical fire on the screen is continually flowing down the screen. Three indirectly accessible fires are produced by the apparatus. Agent application is limited to a horizontal angle of 30 degrees in front of the screen at heights between ground level and 1.52 meters (5 feet). The fire on the back side of the burning ingot and the the pool behind the ingot are shielded from direct agent application by the ingot itself. The fire on the back side of the vertical screen is shielded by the sheet of burning metal and the screen. The horizontal fire behind the base of the screen is shielded by the screen and the metal on the screen.

During medium-scale tests, sections of magnesium ingots weighing approximately 0.91 kilograms (2 pounds) were ignited in the test crucible. Agents were applied from standard portable extinguishers when possible. The results of small- and medium-scale testing are presented in the following paragraphs.

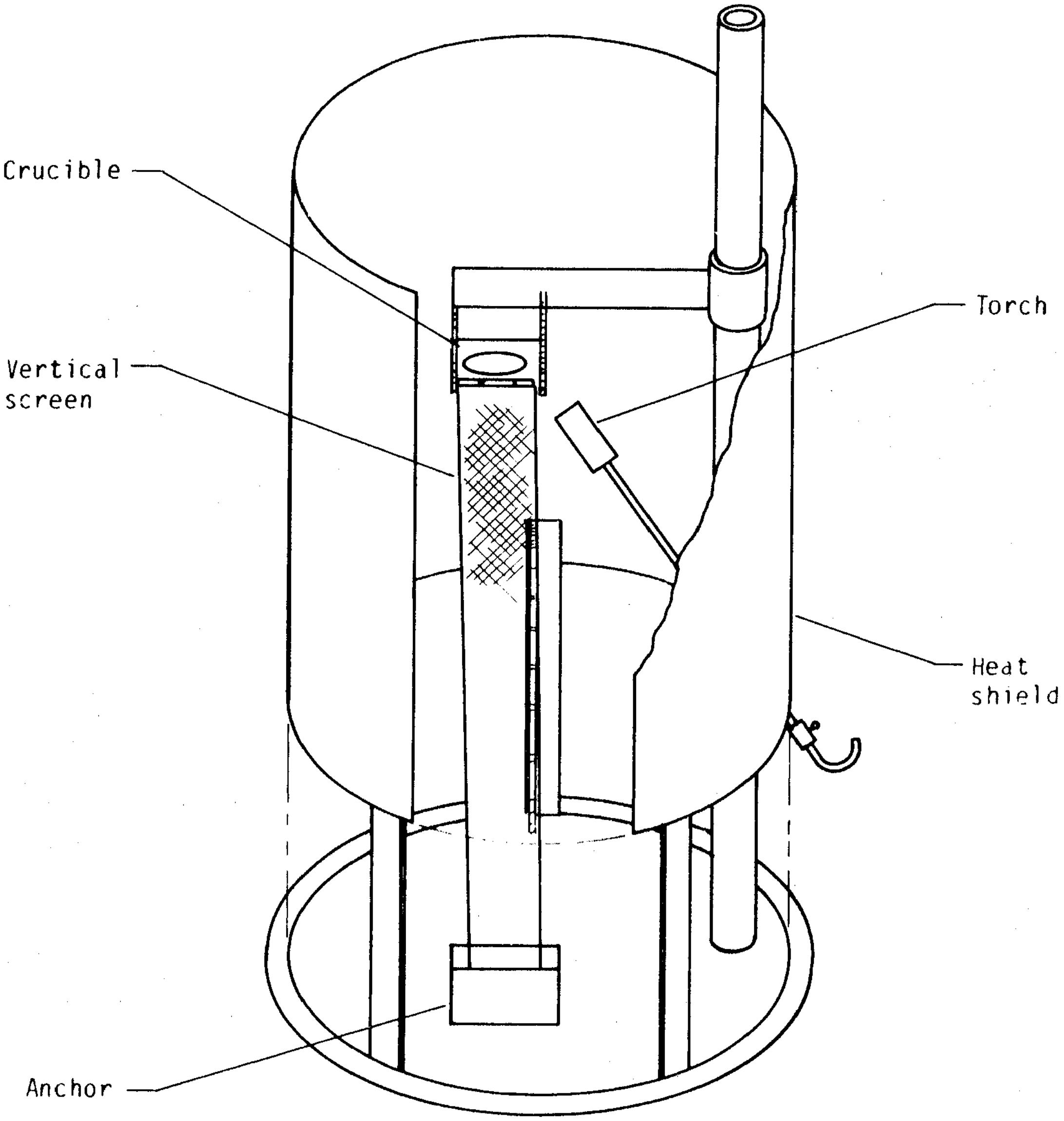


Figure 1. Medium-Scale Test Apparatus.

Test Results

MET-L-X

In small-scale tests on small piles of turnings, MET-L-X was very effective. The fires were covered with a thin layer of agent which completely sealed the surface, extinguishing the fire. No enhancement of the fire occurred as the agent was applied. One characteristic was that the agent would not fuse and seal the fire if the fire was shielded from the agent; this occurred when a burning magnesium chip was located under nonburning chips. The MET-L-X would cover the top of the nonburning chips but would not seal until the adjacent chips began to burn. There was some indication that MET-L-X would adhere to vertical surfaces during small-scale tests.

In medium-scale vertical surface tests, MET-L-X was very effective. The agent adhered to the burning metal on the vertical screen and suppressed the fire immediately. The burning magnesium block and molten pool were also quickly suppressed. The inability of the agent to access indirectly accessible fires was also noted in this test. MET-L-X was applied to the metal fire in the test apparatus from a standard ANSUL 13.61-kilogram (30-pound) portable extinguisher. Approximately 2.27 kilograms (5 pounds) of agent were used during the test. The fire on the vertical screen was completely extinguished with a light covering of agent, leaving the extinguished metal on the screen. The burning block and molten pool appeared to be extinguished quickly with a slightly heavier application of agent. However, a short time after agent application ceased, reignition occurred on the back side of the block where the agent had not been directly applied. The reignition zone expanded, burning back the layer of MET-L-X until the layer reached a certain thickness. The back side of the block was extinguished with repeated application of MET-L-X, but approximately half of the agent used was required to suppress this small area of fire, approximately 5 percent of the total fire area, which was indirectly accessible.

Graphite Powder

Graphite powder was tested only in small-scale fires. Graphite powder controlled the magnesium turning fires, but would not extinguish them in a period of 5 minutes. The burning magnesium would be completely covered by graphite with no outward appearance that the metal continued to burn. Once the graphite blanket was ruptured by stirring, the flames would reappear. There was no indication that the graphite would adhere to vertical surfaces.

Sodium Chloride

Sodium chloride was tested only in small-scale tests. Magnesium turning fires were effectively extinguished with sodium chloride crystals. The pile of turnings was extinguished by a fairly thin layer of sodium chloride. The crystals melted and fused together, sealing the fire from the atmosphere. Most of the magnesium turnings remained unburned. No enhanced reaction occurred when sodium chloride was applied to the fire. The molten covering produced indicates that the agent may work on vertical surfaces.

Dry Chemical Powders

Three dry chemical powders--sodium bicarbonate, potassium bicarbonate, and ammonium--were tested in small-scale tests. Sodium bicarbonate and potassium bicarbonate were tested in large-scale tests. All three powders initially enhanced the combustion of the magnesium in small-scale tests. When enough agent was applied to completely bury the magnesium turnings, the fire burned through the bicarbonates very quickly while the ammonium phosphate continued to control and eventually extinguish the fire. A dark, hard crust formed away from the metal, apparently sealing the metal from the atmosphere, but there was no apparent adhesion to the burnt magnesium turnings. The bicarbonate powders were applied to the large-scale fires primarily to demonstrate the adverse reaction produced.

Talc Powder

Talc was tested only on small-scale fires. The talc reacted slightly with the fire when applied in small amounts. When applied in large quantities the fire was controlled by a thick layer of talc completely covering the pile of turnings. The magnesium continued to burn under the covering of talc until all the magnesium was consumed.

Dry Sand

Sand was tested only on small-scale fires. Prior to testing, the sand was oven-dried for 2 days. The sand reacted with the fire, popping and spattering when applied in small quantities. When the magnesium turnings were completely covered with a pile of sand, the fire was controlled but continued to burn under the sand until all the magnesium was consumed.

Glass Powder

Three forms of glass powders--ground glass powder which passed a Number 200 mesh, glass miscrospheres and glass flakes--were tested on small-scale fires. Only the glass flakes melted and fused to seal the fire from the atmosphere. The other two forms reacted with the fire and would not control it. Although the glass flakes formed a sealed layer over the metal fire and self-healed when the seal was broken, the magnesium was completely consumed.

TMB Liquid

In small-scale testing, TMB proved very effective. From the point of agent volume required to extinguish the 40 ml volume of turnings, the TMB appeared to be the most effective agent tested. Approximately 5 cc were required to extinguish the magnesium turnings fires. When applied, the TMB produces a low-intensity Class B fire which replaces the metal fire almost immediately. The secondary fire is primarily methanol-fueled and burned out quickly after TMB application ceased. TMB produced a white powder coating over the burned metal which bonded the turnings together. A large number of unburned turnings remained after the secondary fire burned out. Reignition of the pile of turnings was very difficult, and the reignited turnings tended to self-extinguish.

Because of its success on the turnings, a small-scale approximation of the medium-scale vertical test apparatus was fabricated under the laboratory hood to test the vertical capabilities of the TMB. Again, the TMB proved very effective, extinguishing the vertical fire very quickly. Some indication was evident that the agent had spread to the back side of a vertical sheet when it was applied to the front side.

Although only 100 ml of TMB remained after the small-scale testing, an attempt to extinguish the medium-scale fire was made. The agent was applied in a small 1.6-millimeter (1/16-inch) orifice straight stream from a distance of 1.22 meters (4 feet). The fire was not completely extinguished; but wherever the agent was applied, the fire was extinguished and did not reignite. The indirectly accessible configuration capabilities indicated in the small-scale test could not be verified in this limited medium-scale test.

Water

In small-scale testing, a fine mist of water increased the intensity of magnesium turnings fires. As the coarseness of the spray and application rate was increased, the aggravation of the fire increased to a point. If the application rate were increased beyond a certain point, the fire would be extinguished. When direct streams or very coarse droplets were applied to the turnings fire, small steam explosions would scatter the turnings.

In medium-scale tests with water, results were mixed. Water was applied to the medium-scale fire using a 25.4-millimeter (1-inch) hose and an adjustable spray nozzle. Flow rate and spray coarseness were adjustable during each test. In some tests, the water spray completely extinguished the metal fire; in other tests, water only enhanced the fire. The method or technique of extinguishing magnesium fires with water is extremely critical to the result. During the limited number of tests performed, a repeatedly effective technique could not be determined. Even when the fires were extinguished, the first effect water application had on magnesium fires was an increase in fire intensity and splattering of burning liquid metal.

AFFF

AFFF was tested on medium-scale magnesium fires, using a solid AFFF cartridge attached to a portable water extinguisher. AFFF had little effect on the metal fire even when a large amount was concentrated on a small area of the fire. An increase in flame intensity and a change in flame color were noted. No suppression of the fire was observed.

Halon 1211 and 2402

The halons reacted violently with the magnesium fires. When a fine mist or halon vapor was applied to the fire, it increased in intnesity significantly. Applying a liquid stream of halon to the magnesium fire caused explosions and scattering of burning metal. Because the small-scale tests indicated such violent reactions, medium-scale testing of halon was deleted from the test plan. Halon 2402 appeared to react more violently than Halon 1211.

Nitrogen (N_2) Liquid

In small-scale tests, liquid N_2 was very effective. Liquid N_2 was poured from a small dewar on piles of burning magnesium turnings. The fire was rapidly extinguished with no initial spattering or increase in fire intensity.

Liquid N_2 proved ineffective in extinguishing medium-scale magnesium fires. Applications of both spray and straight streams were tested. The spray acted much as gaseous N_2, causing an increase in fire intensity. Straight streams of liquid N_2 resulted in vaporization explosions, scatter of burning metal, and an increase in fire intensity.

Silicon Grease

Silicon grease was tested on small-scale magnesium fires. The grease applied in large quantities extinguished piles of burning turnings, forming an airtight seal over the pile. Little melting or adhesion to the burned metal was observed. The grease itself would ignite when applied to an established metal fire but self-extinguished as the metal fire was extinguished. A thick layer of grease applied to the midpoint of a magnesium ribbon prevented a fire on one end of the ribbon from spreading to the other.

Nitrogen (N_2) Gas

Gaseous N_2 produced by the vaporization of liquid N_2 was applied to medium-scale magnesium fires. The result of this application was an increase in fire intensity where the N_2 gas was applied. No suppressing effect was observed.

Carbon Dioxide (CO_2)

CO_2 from a standard CO_2 extinguisher was applied to medium-scale magnesium fires. An increase in fire intensity and a change in flame color were the only effects observed.

PHASE I CONCLUSIONS AND RECOMMENDATIONS

Background information pertaining to burning and extinguishment has been accumulated and reviewed. A list of extinguishing agents suggested for magnesium and other metal fires was generated and a group of the most promising agents for aircraft use were tested on small- and medium-scale fires. The medium-scale tests were carried out on a unique apparatus developed for this effort which repeatedly produces magnesium fires with both vertical and indirectly accessible configurations.

The general requirement for the extinguishment of any fire is that the heat loss, Q_{out}, from the fire must be greater than the heat input to the fire, Q_{in}. Seven categories or approaches to fire extinguishment were presented. The seven categories are as follows:

1. Isolate the fuel.
2. Isolate the oxidizer.
3. Cool the condensed fuels.
4. Cool the gas phase.
5. Blow the flame off the fuel.
6. Inhibit the chemical reaction homogeneously.
7. Inhibit the chemical reaction heterogeneously.

The first five approaches involve physical mechanisms and the last two involve chemical mechanisms. Examples of extinguishing agents which incorporate each of the listed approaches were presented. It was also pointed out that many agents incorporate more than one of these methods to accomplish extinguishment.

Several models for the thermophysical behavior of metal fires, particularly magnesium fires, were presented. All of the models are based on diffusion droplet models, as shown in Figure 2. The rate-controlling phenomenon for magnesium fires appears to be the heat transfer from the standing flame reaction zone back to the fuel surface. Two temperature limits are also present. The flame temperature is limited by the boiling point of the magnesium oxide combustion product; the fuel temperature is limited to the boiling point of the magnesium. The principal homogeneous reaction mechanism in magnesium fires is thought to be the simple dimer ($MgO{\bullet}MgO$) reaction. Several factors combine to make extinguishment of magnesium fires very difficult. The high flame temperature, approximately 7000°F, coupled with the reactiveness of the magnesium, causes many common extinguishing agents to dissociate and actually enhance the combustion process. Water and CO_2 break down and provide additional oxygen to the fire. Nitrogen, normally considered an inerting gas for fire extinguishment, will sustain the combustion of magnesium. The action of halons, which normally slows the combustion process by producing intermediate products which require higher temperatures to react, produces violent reactions at the high temperatures encountered in magnesium fires. The high flame temperature (7000°F), coupled with the high thermal conductivity and low ignition temperature (1200°F) of magnesium, makes extinguishment by cooling very difficult. The entire mass of magnesium involved in a fire will approach the ignition temperature while the flame zone temperature is much higher than that required for combustion. The fact that magnesium ignites at a temperature below the boiling point of the metal indicates that the combustion can take place on the metal surface as well as in the gas phase, indicating a chemical inhibitor would have to function in both burning modes. Most extinguishing agents for metal fires operate by isolating the fuel or oxidizer. The fluxes, powders, and even gases work in this manner. Once the barrier between fuel and oxidizer is established, combustion ceases. The barrier must be maintained for long periods, in some cases several hours, until the fuel has cooled below the ignition temperature.

None of the extinguishing agents identified during this effort can extinguish the general configuration metal fire including suspended vertical and indirectly accessible fires in the open. The gaseous agents boron trifluoride, boron trichloride, and nitrogen reportedly will extinguish general

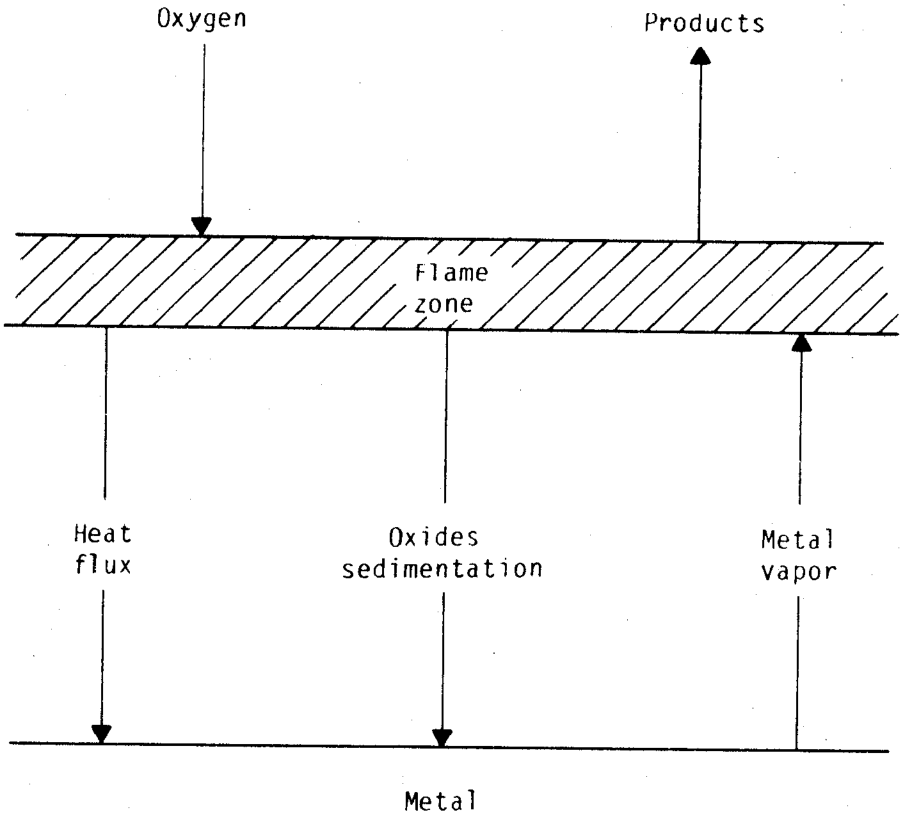


Figure 2. Vapor-Phase Diffusion Flame Model.

configuration fires, but their application is limited to enclosed spaces. The boron gases are also highly toxic. During testing, gaseous nitrogen proved ineffective and actually enhanced combustion.

Several of the agents identified reportedly will extinguish metal fires in the vertical configuration. MET-L-X, TMB liquid, and glass flakes were tested. The MET-L-X and TMB liquid proved very effective against vertical fires in medium-scale tests. The glass flakes controlled the metal fire but would not prevent the magnesium from being consumed.

The remaining agents tested proved either ineffective on horizontal magnesium fires or ineffective on any configuration magnesium fires. Some of the ineffective agents such as the halons actually enhanced the combustion. Table 4 summarizes the agents tested and their performance.

It is recommended that two approaches be taken to arrive at the end product of a general configuration metal fire extinguishant. First, an attempt should be made to reformulate or modify the existing agents which already have the capability of suppressing vertical fires so that they will be capable of extinguishing indirectly accessible fires. This should include an analysis of the existing agent's performance in the field to discover why it has proved inadequate in current applications. This information will be used to assure that the reformulated agent will be able to perform effectively in an operational environment. The initial reformulation direction should be toward a modified carrier to allow the agent to penetrate to indirectly accessible fires by vaporizing or flowing along surfaces.

The second approach should attempt to develop a new formulation. This effort shall take advantage of advances in metal, plasma, and polymer chemistry over the past 20 years to solve the extinguishment problem in a manner different from current agents. Although the homogeneous reaction is not the rate-controlling factor, the suppression of this reaction would assist by slowing heat generation which may allow cooling to be more effective. The alternative to this approach is the forming of a durable barrier between fuel and oxidizer which will withstand heat and disturbances from external sources and will promote cooling.

TABLE 4. PHASE I AGENT TEST SUMMARY.

Agent	Extinguishing mechanism	Scale tested	Effective configuration			Remarks
			Horizontal	Vertical	Indirect	
MET-L-X	Isolation	S, M	Yes	Yes	No	Throw range limited
Graphite powder	Isolation and cooling	S	Yes	No	No	Controlled fire only
Sodium chloride	Isolation	S	Yes	No	No	
Sodium bicarbonate	Chemical and isolation	S, M	No	No	No	Increased fire intensity
Potassium bicarbonate	Chemical and isolation	S, M	No	No	No	Increased fire intensity
Ammonium phosphate	Chemical and isolation	S	Yes	No	No	Coating burned through
Talc powder	Isolation	S	Yes	No	No	Controlled fire only
Sand	Isolation	S	Yes	No	No	Controlled fire only
Glass powder	Isolation	S	No	No	No	Reacted with fire
Glass spheres	Isolation	S	No	No	No	Reacted with fire
Glass flakes	Isolation	S	Yes	No	No	Controlled fire only
TMB liquid	Isolation	S, M	Yes	Yes	No	Secondary fire not intense
Water	Cooling	S, M	Yes/No	Yes/No	Yes/No	Increases fire intensity
AFFF	Isolation and cooling	M	No	No	No	Increases fire intensity
Halon 1211	Chemical	S	No	No	No	Violent reaction
Halon 2402	Chemical	S	No	No	No	Violent reaction
N_2 liquid	Cooling	M	No	No	No	Increased fire intensity
N_2 liquid	Cooling	S	Yes	No	No	Large quantity required
Silicon grease	Isolation	S	Yes	No	No	Large quantity/secondary fire
N_2 gas	Isolation	M	No	No	No	Increased fire intensity
CO_2	Isolation	M	No	No	No	Increased fire intensity

SECTION III

PHASE II--REFORMULATION AND ORIGINATION OF EXTINGUISHING AGENTS

In Phase II of this study, the criteria developed in Phase I were applied in a search for reformulated and new agents capable of extinguishing general configuration metal fires. Two existing agents were evaluated for reformulation. TMB was selected as the primary agent for reformulation. Additives that might improve the basic agent were tested and evaluated in large-scale laboratory testing. The criteria for a satisfactory Class D fire suppressant were refined, and the investigation and preliminary testing of new agent formulations were pursued further.

REFORMULATION

Literature

A thorough search for literature cataloged by the Department of Defense on the combustion of magnesium, aluminum, and titanium and on the extinguishment of metal fires was performed. The facilities of the Defense Technical Information Center (DTIC) were used for this purpose. Abstracts of pertinent papers obtained in that search are presented in Appendix B.

Agents

Selection

In Phase I, MET-L-X, a proprietary dry chemical powder for extinguishment of Class D fires, and TMB, a liquid, boron-containing organic compound, were identified as being particularly effective against magnesium fires in a vertical configuration (Reference 5). These two agents were selected to be considered for reformulation for the purpose of improving their performance. The Air Force currently uses MET-L-X. Two hand-held extinguishers, each containing 9.07 kilograms (20 pounds) of MET-L-X agent, are placed as needed in P-13 airfield ramp fire-fighting trucks. A variety of military and civilian installations have occasionally used TMB as a Class D fire extinguishing agent.

Characteristics

A sodium chloride-based formulation, MET-L-X contains a thermoplastic bonding agent and additives to promote flow and to reduce caking and water absorption. It functions by producing an impervious coating on the fuel surface that excludes oxygen. It absorbs heat from the fuel owing to the heat capacity of the inert salt and the latent heat of fusion of the thermoplastic. The thermoplastic forms a matrix to support the salt and to bond it to the metal fuel surface so that it can operate against fires in a vertical configuration. The limitations of MET-L-X, as it is currently used in Air Force delivery systems, are the following:

1. It has a limited throw range, particularly in crosswind or headwind situations.

2. It has an exceedingly limited capability against indirectly accessible fires.

3. It has a marginal coating integrity. The coat formed to isolate the fuel from air is inconsistent in quality and is not durable when cooled by water.

4. The quantities currently carried in Air Force vehicles are inadequate for suppressing large aircraft magnesium fires.

MET-L-X has a number of desirable characteristics. Its toxicity is low; its reactivity is low (no secondary fire and no reaction with metal fuel); it is easily handled; it has a long shelf life; it provides some cooling capability; and it is relatively inexpensive ($0.71/0.4536 kilogram [pound]).

TMB liquid is a commercial chemical that has been tested and occasionally used as a Class D fire-extinguishing agent. It is formed by allowing trimethyl borate and boric oxide to react at high temperature and pressure (Equation 1).

$$B_2O_3 + B(OCH_3)_3 \rightarrow B_3O_3(OCH_3)_3 \qquad (1)$$

The resulting product is believed to consist primarily of a compound having the molecular structure shown in Figure 3. Undoubtedly, however, there is a significant association between molecules and some polymeric structure. In the presence of hydrolysis and loss of volatiles, additional compounds are present. It has been reported that TMB is a highly effective extinguishing agent for metal fires. Cleanup after using TMB is no more involved than it is when dry powders are used, and toxicity problems appear to be minimal.

In the presence of heat, thermal decomposition occurs, and methanol (which will burn in a fire) and boron trioxide are formed.

$$B_3O_3(OCH_3)_3 \rightarrow B_2O_3 + B(OCH_3)_3 \qquad (2)$$

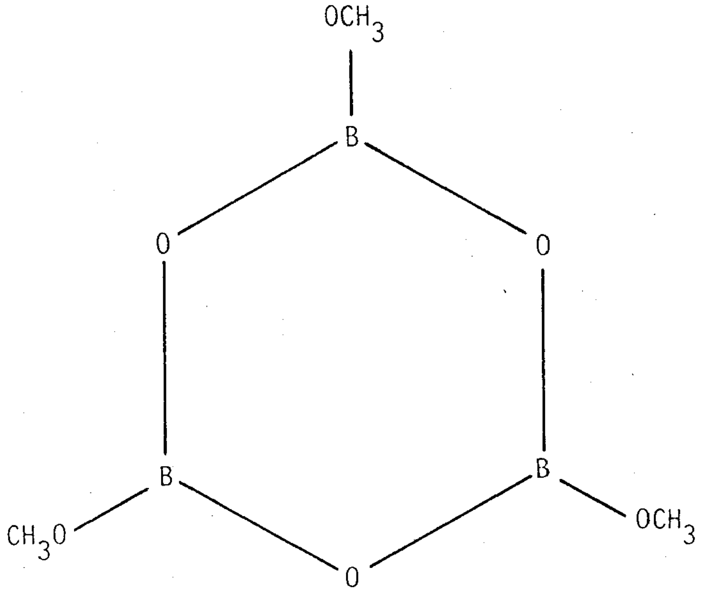


Figure 3. Molecular Structure of Trimethoxyboroxine

It has been assumed that in metal fire extinguishment, the boric oxide residue fuses on the metal surface to form a coating that excludes oxygen. Some evidence indicates, however, that compounds other than boric oxide are also formed at magnesium surfaces, as will be pointed out later in this section. Such additional reactions may explain the highly effective surface-inerting properties of TMB. Although TMB is a very effective extinguishing agent, it does have some drawbacks. Among these are the following:

1. Because TMB is a flammable liquid, it presents shipping, handling, and storage problems.

2. It produces a secondary Class B fire during extinguishment of Class D fires. The secondary fire is due, at least in part, to flammable methanol released during the thermal decomposition of TMB.

3. It is susceptible to hydrolysis, which produces a precipitate that can interfere with the delivery system by plugging nozzles and valves. When TMB was used by the United States Navy, the extinguishers required an inordinate amount of maintenance and, even then, were unreliable. Even slow TMB leaks or seepage past the main release valve of the converted water extinguisher produced a crystalline deposit in the valve throat, which restricted or prevented the release of the agent even when the pressure gage showed a full charge. Consequently, the extinguisher and valve mechanism had to be disassembled frequently and deposits cleaned out of the valve. Even after the mechanism had been reassembled, no one could be certain that the extinguisher would work a day or a week later.

4. On open-air aging or at low temperatures, TMB may exhibit unacceptably high viscosities.

5. The toxicity of TMB and its combustion products, although low, is larger than that of MET-L-X.

6. It degrades certain polymeric materials.

7. It is relatively expensive ($4.25/0.4536 kilogram [pound] for industrial grade).

Reformulation Objectives

Modifications to both TMB and MET-L-X were carefully considered. The latter agent suffers from two major problems. First, MET-L-X is a solid powder and therefore has a limited throw range, poor applicability in indirectly accessible fires, and inferior application properties under windy conditions. Second, MET-L-X has only fair surface-inerting properties, apparently as a result of the poor integrity of the surface formed on fusion. The surface often has large gaps where burning continues or where reignition occurs. Reformulation of MET-L-X would require that its physical state be modified so as to change its application properties. Combining the agent with a liquid to form a slurry could improve the throw; however, most liquids are either reactive toward hot magnesium fuel or toward oxygen. Moreover, there would always be a potential problem with phase separation. The thermoplastic could be modified to increase flow and spreading so as to improve the surface integrity and inerting properties. This approach, however, requires formulation with new polymeric systems, a long and difficult task at best. Owing to the complexity of the agent and the fact that MET-L-X is unsatisfactory, basically because it is a solid, a decision was made to focus attention on TMB, which is already in the desired liquid state and has a well-defined composition.

Four basic problems must be addressed in modifying TMB or in designing a functioning application system:

1. Flammability.
2. Viscosity.
3. Hydrolysis and aging characteristics.
4. Compatibility with polymers.

Reformulation and Lab Testing of TMB

Flammability

Halon 2402 was added to TMB in a successful attempt to reduce the flammability. Reducing the flammability reduces the handling, shipping, and storage hazard. It may also reduce the secondary fire (possibly resulting from the formation of methanol) produced when TMB is applied to burning magnesium. It could also facilitate the use of a TMB fog to reach fires that are not directly accessible without causing flashback. A potential problem, however, is that Halons are reactive toward hot magnesium metal, with which they form magnesium halides. Reactions of halogenated hydrocarbons with burning magnesium are often violent.

In a series of magnesium fire extinguishment tests, a medium-scale configuration (Reference 5) was used, and TMB was applied with 0-, 10-, and 25-percent by volume Halon 2402. MET-L-X was also applied. The purpose of these tests was to establish a baseline performance for TMB in the standard general-configuration magnesium fire, to compare the performance of TMB to that of MET-L-X, and to determine the effects on the performance of TMB produced by the addition of Halon 2402. Multiple tests were performed in which TMB and a mixture of 90-percent TMB and 10-percent Halon 2402 was used. Single tests were performed in which 75-percent TMB with 25-percent Halon 2402 and MET-L-X were used. In some tests the propane torches remained on during extinguishment; in other tests they were turned off after the magnesium ignited. In all tests, a water spray was applied to the magnesium after the intense magnesium flame had been suppressed. The fuel in each test was a magnesium ingot having a mass of approximately 1 kilogram (2 pounds). The TMB-based agents were applied by a standard 9.5-liter (2.5-gallon) water extinguisher pressurized to 862 kPa (125 lb/in^2). The MET-L-X was applied by a standard 9.1-kilogram (20-pound) MET-L-X extinguisher. A summary of the quantities required for extinguishment is presented in Table 5.

All of the TMB agents proved to be effective extinguishants. In fact, the medium-scale, general-configuration magnesium fire was insufficient to test the limits of the capabilities of the TMB-based materials. Tests were conducted in winds up to approximately 40 km/h (25 mi/h). At times the winds were perpendicular to the direction of agent application. The straight-stream nozzle directed the agent on target from 6 meters (20 feet) away. The maximum distance was limited by the test facility, not by the agent or by the extinguisher. On the other hand, the MET-L-X powder failed to extinguish the indirectly accessible portions of the magnesium fire even under conditions that seemed extremely favorable to its use. During the single test in which MET-L-X was used, a 32-km/h (20-mi/h) wind blew directly from the extinguisher operator to the test fire, carrying the powder to the fire with very little loss. The apparatus enclosure trapped the delivered MET-L-X agent and held a dense powder cloud around the magnesium fire for 45 to 60 seconds. The directly accessible portions of the fire, including the vertical sections, were extinguished when approximately one-half of the 9.1-kilogram (20-pound) supply of agent had been expended; however, the areas not directly accessible were not extinguished even in the extended presence of the cloud of MET-L-X powder.

TABLE 5. AVERAGE WEIGHT OF AGENT REQUIRED TO EXTINGUISH A MEDIUM-SCALE MAGNESIUM FIRE.

Fire condition	Weight, kg			
	TMB	90% TMB-10% 2402	75% TMB-25% 2402	MET-L-X
Torch on	2.1	1.7	4.2	[a]>9.1
Torch off	1.5	1.4	[b]---	[b]---

[a] The entire contents (9.1 kg) of the MET-L-X extinguisher was expended without extinguishing the indirectly accessible regions of the burning magnesium.

[b] Not tested under this condition.

The results of these tests showed that the presence of 10-percent Halon 2402 in the TMB did not interfere with the metal-fire-extinguishing capabilities of the TMB. On the other hand, at a 25-percent Halon concentration, violent reactions occurred and more than twice as much agent was required for extinguishment. To determine the optimum amounts of Halon 2402 additive, additional magnesium fire-extinguishment experiments were run. The results showed that 10-percent by volume Halon 2402 was the maximum amount allowable. Above that amount, a vigorous reaction occurred.

Attempts were made to determine the flashpoints of TMB-Halon mixtures by using a Penske-Martin closed cup apparatus; however, the attempts proved unsuccessful because the Halon 2402 vapor extinguished the ignition flame. Qualitative tests showed that in open containers, even when the mixture was heated for brief periods or when ignition was attempted with a propane torch, TMB with 10-percent by volume Halon 2402 could not be ignited. Heating for extended periods would, of course, cause sufficient loss of Halon that the agent could be ignited; however, even in this case, the fire was feeble and easily extinguished. Pure TMB ignited easily and burned vigorously with a green flame under all conditions.

To test flashback characteristics, nozzles were used to produce a variety of droplet sizes and spray patterns, which were applied to medium-scale magnesium fires. In none of these tests did either TMB or TMB-Halon mixtures flash back from the fire.

From these results, the following can be concluded:

1. The addition of Halon 2402 at the 10-percent level significantly reduces the flammability of TMB.

2. Neither TMB nor TMB-Halon mixtures produced any readily observed flashback problem.

Viscosity

At low temperatures (or after prolonged standing), TMB may exhibit a sufficiently high viscosity that application becomes difficult. A qualitative test of the viscosity characteristics of TMB and TMB-Halon 2402 mixtures at low temperatures was performed. Samples of TMB and TMB with 10-, 15-, and 25-percent Halon 2402 were cooled to -25°C for 24 hours. The samples were then examined for signs of separation and tipped to disclose differences in viscosity. No signs of separation or precipitation were apparent in any of the solutions and, as expected, the higher the Halon content of the solution, the lower the apparent viscosity. The consistencies of the samples ranged from tar-like for straight TMB to watery for TMB with 25-percent Halon.

Viscosities were measured at 24°C on a Brookfield Model LVTD viscometer. The viscosity of TMB was determined to be 25.5 centipoises; that of TMB with 10-percent Halon 2402 was 17.5 centipoises.

From these results, it was concluded that the addition of Halon 2402 significantly improves the viscosity and low-temperature fluidity (and, therefore, the handling and application properties) of TMB.

Hydrolysis and Aging Characteristics

In contact with air, TMB exhibits a marked increase in viscosity and forms a white crust. Chemical analysis of the crust indicates that it is primarily boric acid, H_3BO_3:

	Found	Calculated for H_3BO_3
C, %	<0.7	0
H, %	5.05	4.89

The changes in physical properties appear to be due to two processes. First, owing to the presence of water in the air, hydrolysis occurs with a loss of methanol, CH_3OH, and the formation of boric acid, H_3BO_3 (Reference 2):

$$B_3O_3(OCH_3)_3 + 6H_2O \rightarrow 3H_3BO_3 + 3CH_3OH \qquad (3)$$

A second cause of the changes with aging in the presence of air is the loss of one or more volatile components over and above the methanol formed during hydrolysis. The volatile material lost contains boron (as shown by the formation of boric acid during the hydrolysis of the volatile component itself) and is most probably trimethylborate (trimethoxyboron), $B(OCH_3)_3$. The TMB breaks down into trimethylborate and boron trioxide when it is heated (Equation (2), Reference 6), and it is probable that this same reaction occurs even at ambient temperatures, albeit at a slower rate. The loss of methoxy groups, either as trimethylborate in this reaction or as a methanol following hydrolysis, is expected to increase the amount of crosslinking and,thus,to increase the viscosity of the mixture.

Three potential additive mechanisms were proposed to decrease the changes exhibited by TMB as a result of hydrolysis and volatilization:

1. Additives that react with water could remove water from the system before hydrolysis of the TMB occurs.

2. Acidic additives would lower the pH and thereby reduce the rate of hydrolysis. Owing to the large nucleophilicity of the hydroxide ion, bases exert a significant catalytic effect in hydrolytic reactions (Reference 7).

3. Agents that complex the boron should reduce the loss of volatile boron compounds (by increasing their molecular weight) and at the same time reduce the amount of crosslinking.

To evaluate various additives, two tests were conducted. In one, a mixture of TMB and additive was coated on a glass slide, the slide was placed in a desiccator containing water vapor, and the time to formation of a white coating was observed. In the second test, the viscosity of mixtures of additive and TMB was followed as a function of time. Among the additives tested were glycerol, ethylene glycol, and dulcitol, which are expected to be good boron-complexing agents. They are oxygen-containing liquids and should bind boron readily. D-glucuronic acid is a complexing agent; it is also acidic and lowers the pH of its solutions. Finally, alpha-D-glucoheptanoic acid gamma-lactone and gamma-gluconolactone are complexing agents. They are reactive toward water, and acidic products are formed in that reaction. Despite their optimal properties, none of these additives produced any significant improvement of the aging-in-air characteristics of TMB.

At this point, aging tests were initiated on TMB with silicone oils. Dow Corning 510 (phenylmethyl polysiloxane, 50-centistoke viscosity) and 200 (dimethyl polysiloxane, 5- and 20-centistoke viscosities) silicone fluids were tested as additives. In addition, TMB containing Halon 2402 was evaluated. In the initial studies, viscosities as a function of time were determined for mixtures containing 1 percent silicone fluid by weight or 10 percent Halon 2402 by volume. Viscosities were determined on approximately 400 mL of sample. A Brookfield Model LVTD viscometer at ambient temperatures (20 to 27°C) was used for this purpose. Although viscosity depends strongly on temperature, the use of a TMB control containing no additive eliminated the need for a controlled-temperature environment. The mixtures were allowed to sit in open containers in a closed fume hood with the fans running. The aging tests were terminated at 90 hours for the mixtures containing silicones and at 335 hours for the TMB control and the TMB-Halon 2402 mixture.

The results (Table 6) of these viscosity tests with silicone or 2402 additives were surprising. It was expected that the silicone fluids would cover the surface and inhibit both the entry of water vapor and the loss of volatile components. In addition, the silicone oils were expected to decrease viscosity and improve flow characteristics owing to their lubricant properties. On the other hand, Halon 2402 should evaporate from an exposed mixture relatively rapidly, after which time it should have no effect. However, the addition of silicone fluid caused a marked increase in the aging viscosity, and the addition of 2402 gave improved viscosity properties with aging. The relative effectiveness of the various additives is best seen in Figures 4 and 5. Note that the viscosity in Figure 4 is graphed on a log scale. Some of the variation shown in Figure 5 is a result of temperature variation; undoubtedly, however, the addition of 2402 at the 10-percent by volume level significantly improves the aging performance for viscosity.

In hopes of explaining these seemingly anomalous results, additional aging experiments were conducted, monitoring weight loss rather than viscosity. The purpose was to determine whether the viscosity changes were correlated with the loss of volatile components. In the initial series of experiments (Study 1), the weight losses on aging were determined for mixtures of TMB with 0.5-, 1-, 2-, 5-, and 10-percent by weight Dow Corning 200 silicone fluid (5-centistoke viscosity) and with 2-, 5-, 10-, and 20-percent by volume

TABLE 6. VISCOSITY CHANGES ON OPEN-AIR AGING OF MIXTURES OF TMB WITH SILICONE FLUIDS OR HALON 2402.

Additive	Viscosity, cP												
	0 h	18 h	25 h	42 h	49 h	66 h	90 h	162 h	187 h	217 h	239 h	264 h	335 h
None (control)	25.5	36.5	26.5	34.5	33.0	38.5	44.0	65.0	63.0	46.0	50.0	55.0	53.5
200 (5 cSt)	22.5	106.0	111.5	522.0	604.0	190.2	477.0	Test terminated at 90 h					
200 (20 cSt)	24.5	51.0	42.0	94.0	92.0	197.0	440.0	Test terminated at 90 h					
510 (50 cSt)	25.0	45.5	40.0	80.0	77.5	167.0	367.5	Test terminated at 90 h					
2402	17.5	21.5	17.5	20.0	18.0	19.5	20.0	26.5	26.0	21.5	21.5	21.0	21.0

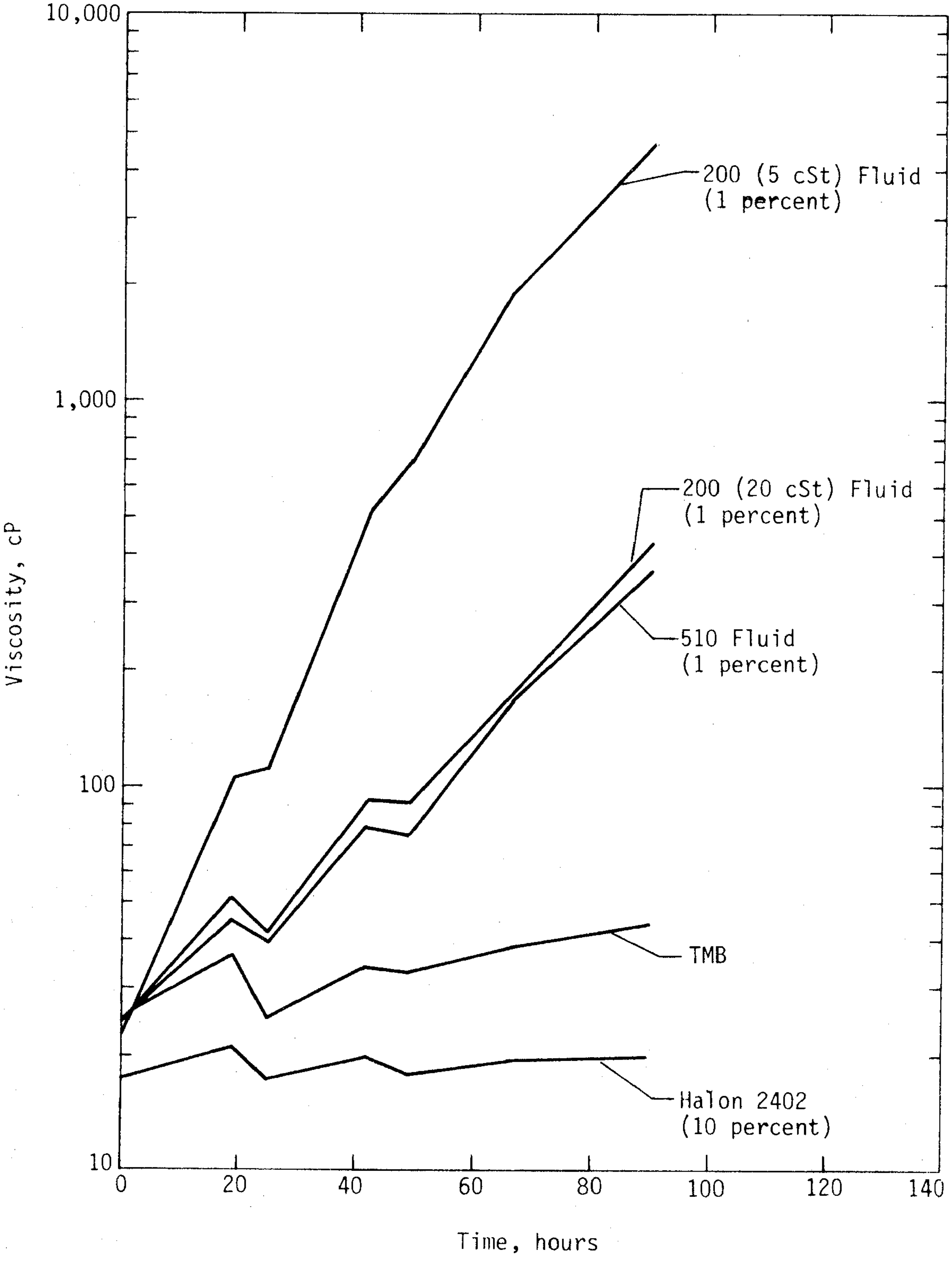


Figure 4. Viscosity in Centipoise as a Function of Time for Open-Air Aging of TMB with Various Additives.

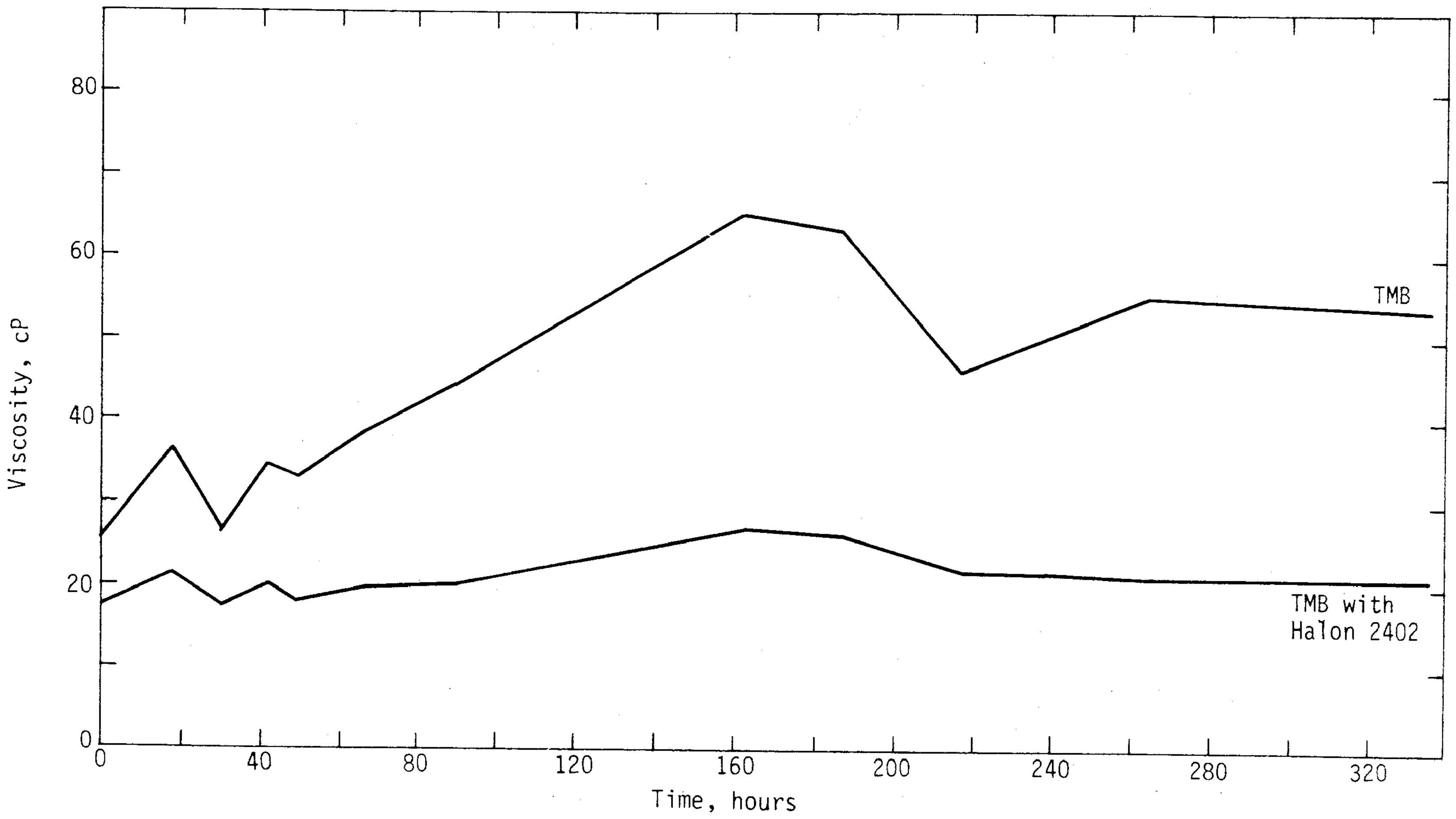


Figure 5. Viscosity in Centipoise as a Function of Time for Open-Air Aging of 90 Percent TMB with 10 Percent Halon 2402 and TMB Control.

Halon 2402. The procedure employed previously was used to age the mixtures to a maximum of 192 hours. Simultaneous monitoring of the samples for viscosity was not performed owing to an unavoidable loss of sample during the viscosity determinations. The results of this first study are presented in Table 7 and in Figures 6 and 7. When a low level of Dow Corning 200 silicone fluid is added, an initially rapid weight loss, and then a more moderate loss, occurs. With larger amounts of silicone additive, the initial weight loss is somewhat lower. The addition of 2402 to TMB gives weight loss-time curves that are different from those obtained with TMB and silicone fluid. The initial, more rapid loss in weight is much lower than that obtained for the addition of silicone fluid. Furthermore, the plateau is reached much sooner and at a much lower percentage loss (except possibly for the lowest amount of Halon 2402 added).

TABLE 7. WEIGHT LOSS ON OPEN-AIR AGING OF MIXTURES OF TMB WITH 5-cSt-VISCOSITY SILICONE FLUID OR WITH HALON 2402 (STUDY 1).

Additive	Weight loss, percent					
	18 h	46 h	70 h	95 h	167 h	192 h
2% 2402	0.70	1.07	1.44	5.54	7.84	7.87
5% 2402	0.60	0.60	0.60	0.76	0.76	0.83
10% 2402	1.28	1.37	1.37	1.76	1.85	1.92
20% 2402	2.15	2.25	2.33	3.00	3.55	3.67
1/2% 200 fluid	8.65	11.27	11.35	11.37	11.45	11.50
1% 200 fluid	4.90	9.64	11.52	12.37	14.09	14.26
2% 200 fluid	2.63	6.55	8.95	10.20	13.18	13.95
5% 200 fluid	1.05	2.65	4.05	5.10	7.55	8.63
10% 200 fluid	0.35	1.15	1.85	2.50	4.25	4.95

A comparison of the effect of adding silicone fluid to that of adding Halon 2402 is best seen in Figure 8, which shows the weight loss at the end of the test (192 hours) as a function of the percent by volume Halon 2402 and percent by weight Dow Corning 200 silicone fluid. As in the case of aging changes monitored by viscosity, Halon 2402 gives much better aging properties than does silicone fluid. The slopes (but not the magnitudes) of the curves

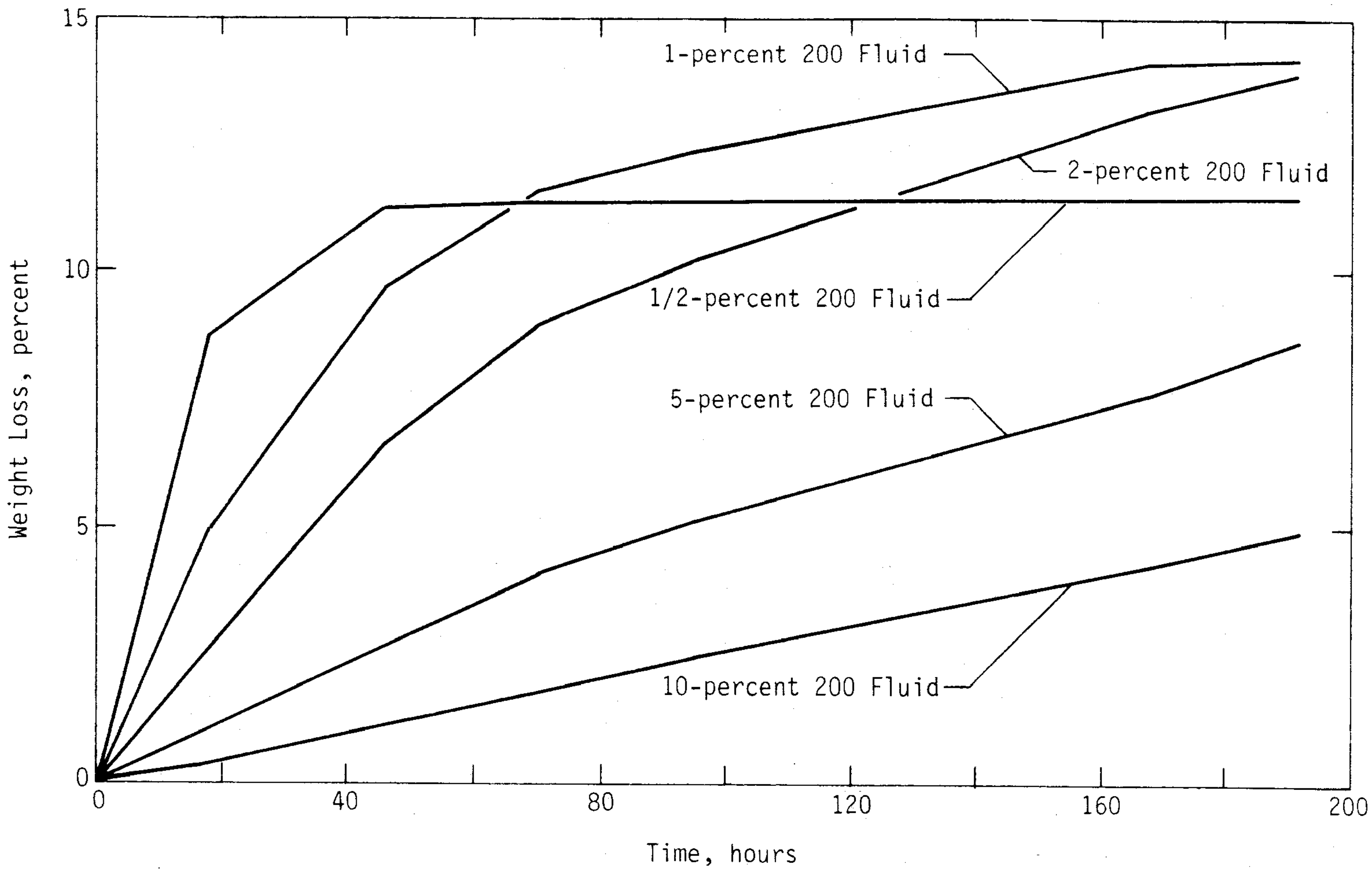


Figure 6. Weight Loss as a Function of Time for Open-Air Aging of TMB with Varying Amounts of Silicone Fluid (Study 1).

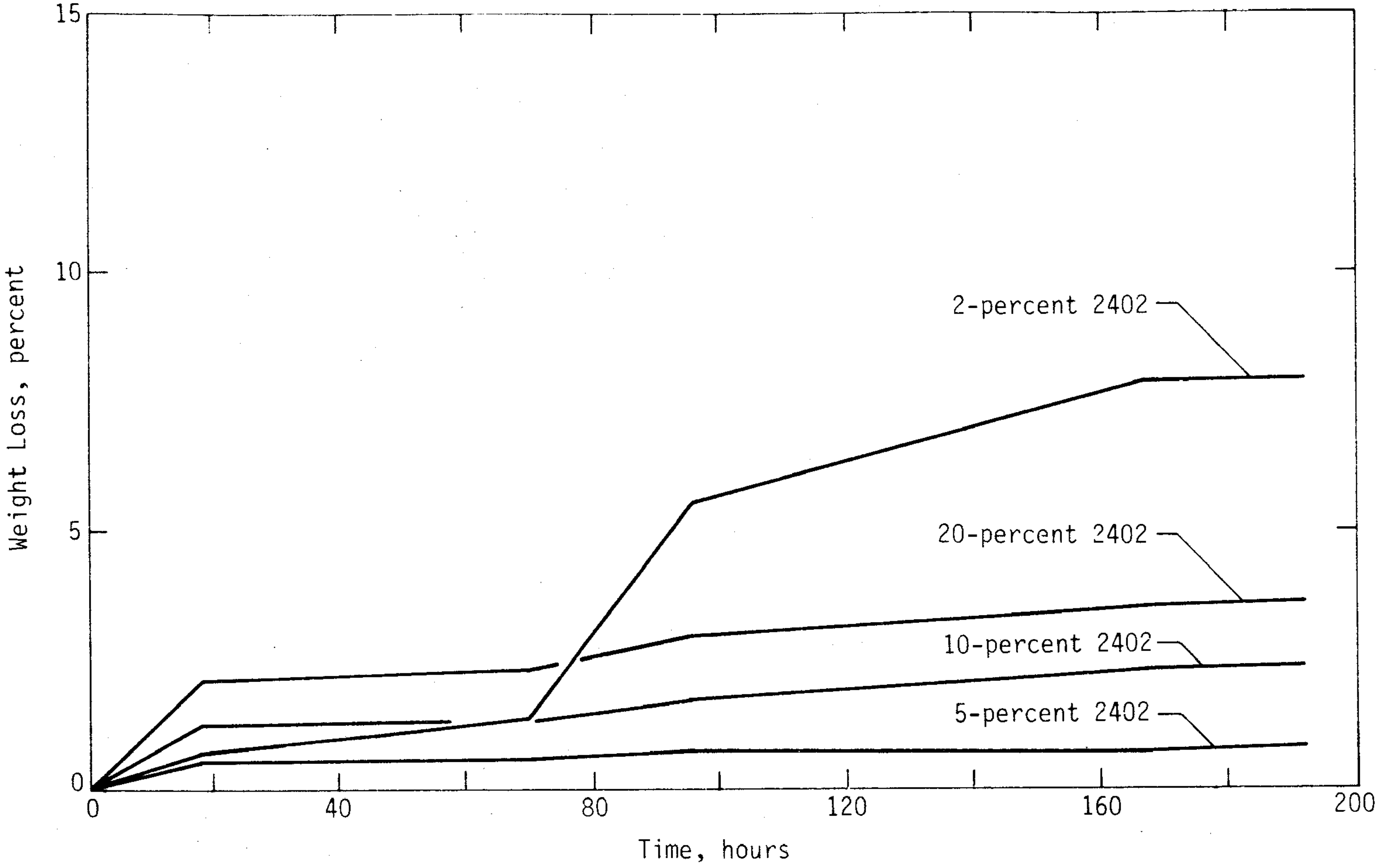


Figure 7. Weight Loss as a Function of Time for Open-Air Aging of TMB with Varying Amounts of Halon 2402 (Study 1).

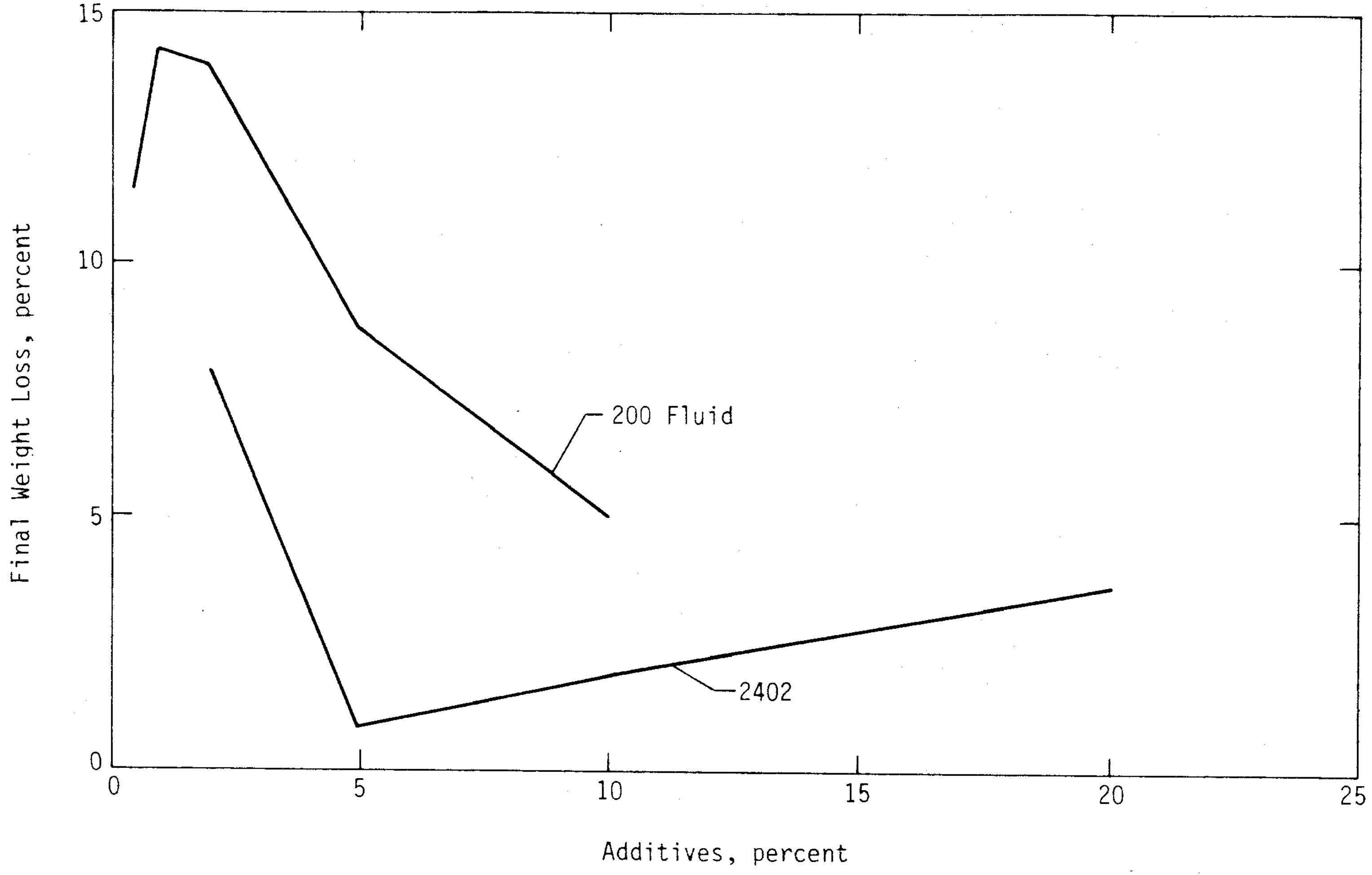


Figure 8. Weight Loss for TMB-Additive Mixtures as a Function of Additive Amount After 192 Hours of Open-Air Aging (Study 1).

shown in Figure 6 at higher percentages of additive are easily explained. Silicone fluids are not miscible with the TMB and float on the surface. The vapor pressure of 5-centistoke-viscosity Dow Corning 200 silicone fluid is much less than that of TMB (at 38°C, TMB: approximately 100 torr [Reference 2]; 5-centistoke Dow Corning 200: approximately 0.1 torr [by extrapolation of data obtained from Dow Corning]). Therefore, the silicone fluid can act as a barrier to volatilization from the TMB surface. As more silicone fluid is added, it acts as an increasingly effective barrier to the loss of volatiles. On the other hand, Halon 2402, which is miscible in TMB, has a very high vapor pressure (about 341 mm Hg at 25°C; Reference 8). At higher concentrations, the vapor pressure of the mixture is increased with increasing Halon 2402 concentration. Neither of these considerations, however, explains the actions of silicone fluid and Halon 2402 at lower concentrations, where the addition of silicone has an increasingly detrimental effect and the addition of Halon 2402 an increasingly beneficial effect.

The results were sufficiently surprising that the weight loss experiment was rerun. A somewhat different range of additive amounts was used, and TMB controls were employed (Study 2). Separate controls were employed for the Halon and silicone fluid additive experimental runs owing to slight differences in the total volumes of liquid used. Mixtures of TMB with 0-, 0.5-, 1-, 2-, 5-, and 10-percent by weight, 5-centistoke Dow Corning 200 silicone fluid and with 0-, 2-, 5-, 10-, and 20-percent by volume Halon 2402 were allowed to sit in open containers in a fume hood with air circulation for 502 hours. The results are presented numerically in Table 8 and graphically in Figures 9 and 10. These figures show something that had not been evident before (owing to the lack of control): TMB without additives suffers a rapid initial loss of weight. Comparison of these data with the viscosity changes shows that this rapid loss of weight is not reflected in a similar rapid increase in viscosity (Figure 5), although the overall trend for both viscosity and weight loss is an increase with time. Thus, these data indicate that although the viscosity changes in pure TMB on open-air aging may be due both to loss of volatiles and to hydrolysis, the latter is probably more important (the slope of the viscosity-time curve is far more constant--excluding short-term variations due to temperature fluctuations--than is the slope of the weight loss-time curve, which shows a steep increase followed by a plateau). Note that hydrolysis alone must lead to a weight gain, which would vary in magnitude depending on

TABLE 8. WEIGHT LOSS ON OPEN-AIR AGING OF MIXTURES OF TMB WITH 5-cSt VISCOSITY SILICONE FLUID OR HALON 2402 (STUDY 2).

Additive	Weight loss, percent													
	24 h	95 h	120 h	145 h	168 h	192 h	264 h	289 h	313 h	337 h	360 h	433 h	457 h	502 h
None (control)	9.82	9.58	9.60	9.65	9.72	9.70	9.63	9.75	9.72	10.41	10.39	10.32	10.29	10.27
2% 2402	1.69	1.59	1.90	2.11	2.32	2.46	2.55	2.95	3.16	3.63	3.75	3.82	3.93	4.10
5% 2402	1.58	1.51	2.66	3.20	4.03	4.21	4.44	5.79	6.11	6.50	6.82	6.96	7.00	7.14
10% 2402	1.52	1.49	2.14	2.50	2.65	2.68	2.72	3.28	3.39	3.41	3.43	3.46	3.46	3.48
20% 2402	2.24	2.58	3.72	4.11	4.30	4.32	4.42	5.13	5.15	5.15	5.17	5.17	5.19	5.21
1/2% 200 fluid	10.38	10.73	10.81	11.03	11.08	11.11	11.18	11.21	11.21	11.21	11.23	11.23	11.23	11.23
1% 200 fluid	6.42	12.42	12.75	12.85	12.87	12.92	13.00	13.00	13.02	13.02	13.07	13.07	13.07	13.07
2% 200 fluid	3.45	9.73	10.83	12.05	12.85	13.50	13.90	13.98	14.00	14.03	14.05	14.10	14.13	14.18
5% 200 fluid	1.47	5.15	6.07	7.42	8.00	8.75	9.77	10.30	10.72	11.27	11.70	12.10	12.35	12.62
10% 200 fluid	0.75	2.10	2.80	3.50	4.12	4.60	5.42	6.02	6.45	6.77	7.30	8.00	8.35	8.75
None (control)	7.20	7.12	7.30	8.05	8.05	8.10	8.02	8.05	8.07	8.07	8.07	7.97	7.95	7.95

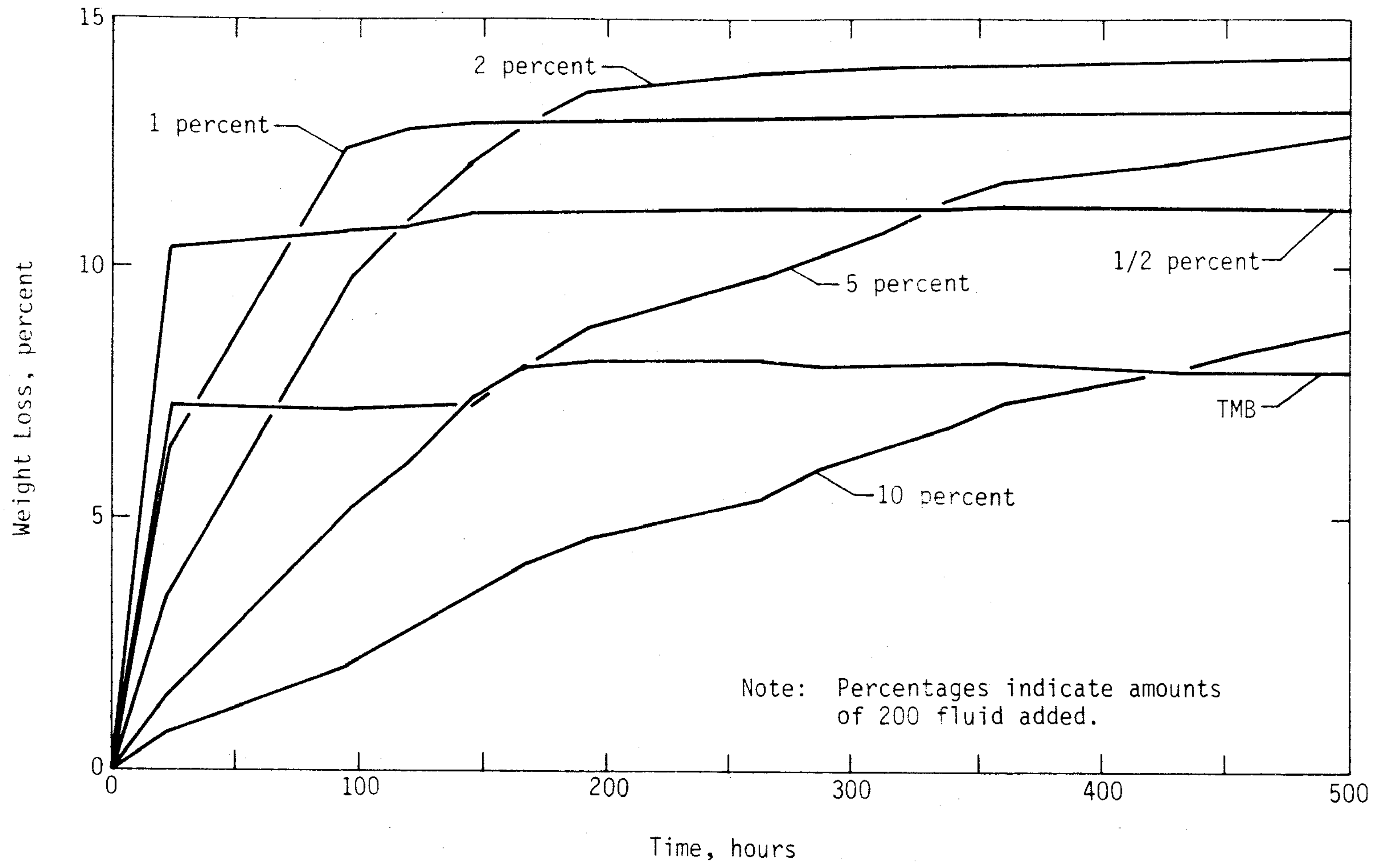


Figure 9. Weight Loss as a Function of Time for Open-Air Aging of TMB with Varying Amounts of Silicone Fluid (Study 2).

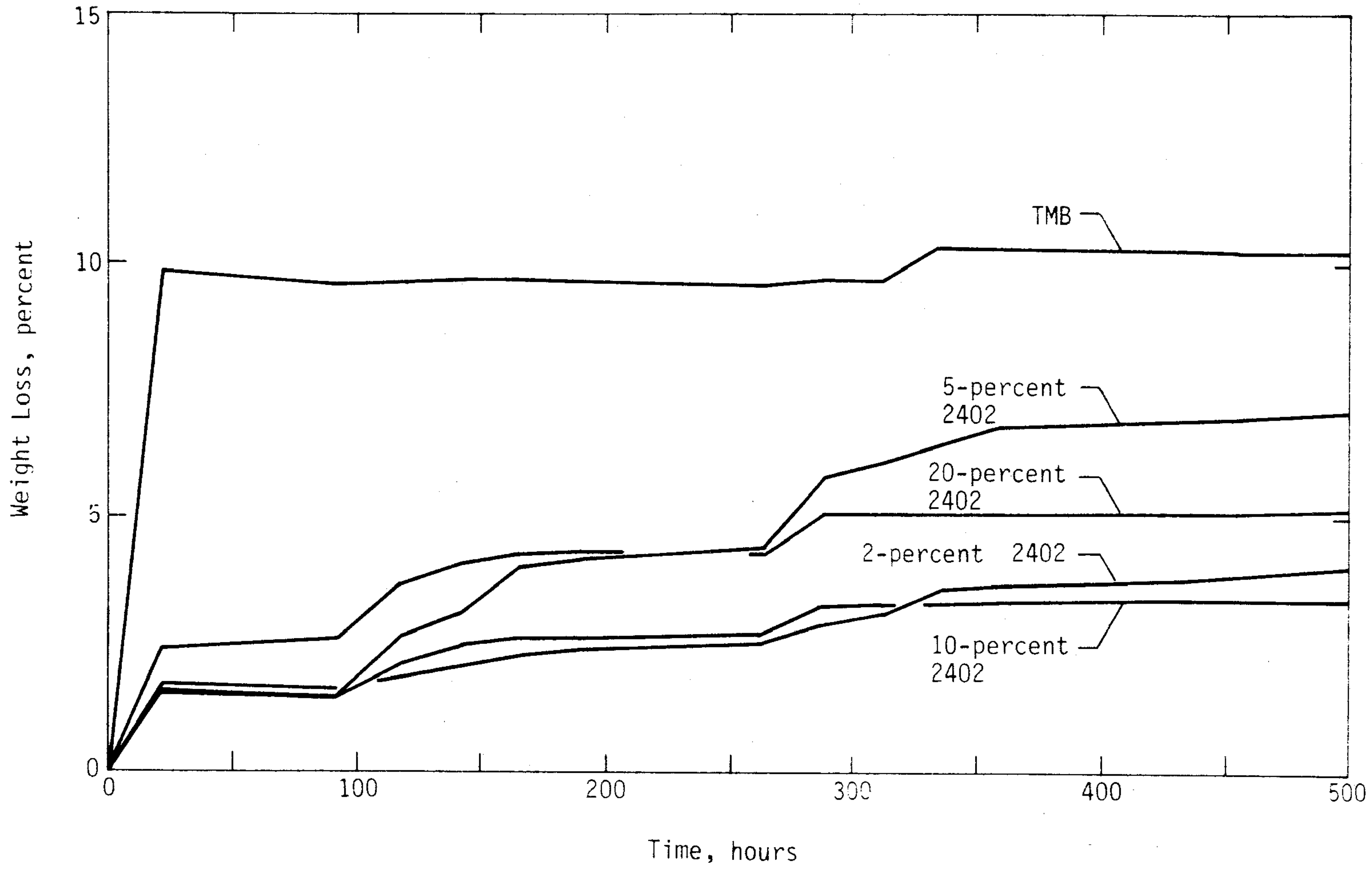


Figure 10. Weight Loss as a Function of Time for Open-Air Aging of TMB with Varying Amounts of Halon 2402 (Study 2).

whether the methanol formed is volatilized. The addition of both Halon 2402 and silicone fluid decreases the rapid initial weight loss, although the Halon is considerably more effective in this regard. However, the TMB-silicone mixtures continue to lose weight long after the TMB and TMB-Halon mixture weight-time curves have reached a plateau.

The weight losses as functions of amount of additive for TMB-silicone and TMB-Halon are shown in Figure 11. The relationships are similar to those shown in Figure 8, although there are some irregularities in the TMB-Halon curve. Again the addition of silicone fluid gives an increased weight loss on aging, and the addition of Halon 2402 gives a decreased weight loss, intermediate amounts of additive being the most "effective" (i.e., beneficial for Halon and deleterious for silicone fluid).

No explanation for the observed effects with Halon 2402 and silicone fluid additions is readily apparent, but one can draw the following conclusions:

1. On setting in air, TMB forms a crust, undergoes a relatively slow increase in viscosity, and exhibits an initially rapid decrease in weight. These changes are due to hydrolysis and loss of volatiles.

2. The addition of Halon 2402 (optimum amount is around 10 percent) to TMB significantly decreases the viscosity gain and the weight loss on aging and therefore improves the aging properties of TMB.

3. The addition of silicone fluid to TMB causes a large rise in the rate of viscosity increase and in the overall weight loss. These are both deleterious changes.

Compatibility Studies

In the initial TMB studies, it was observed that the TMB agent severely attacked a plastic dip tube in a fire extinguisher. A series of compatibility studies was carried out to determine which materials could be

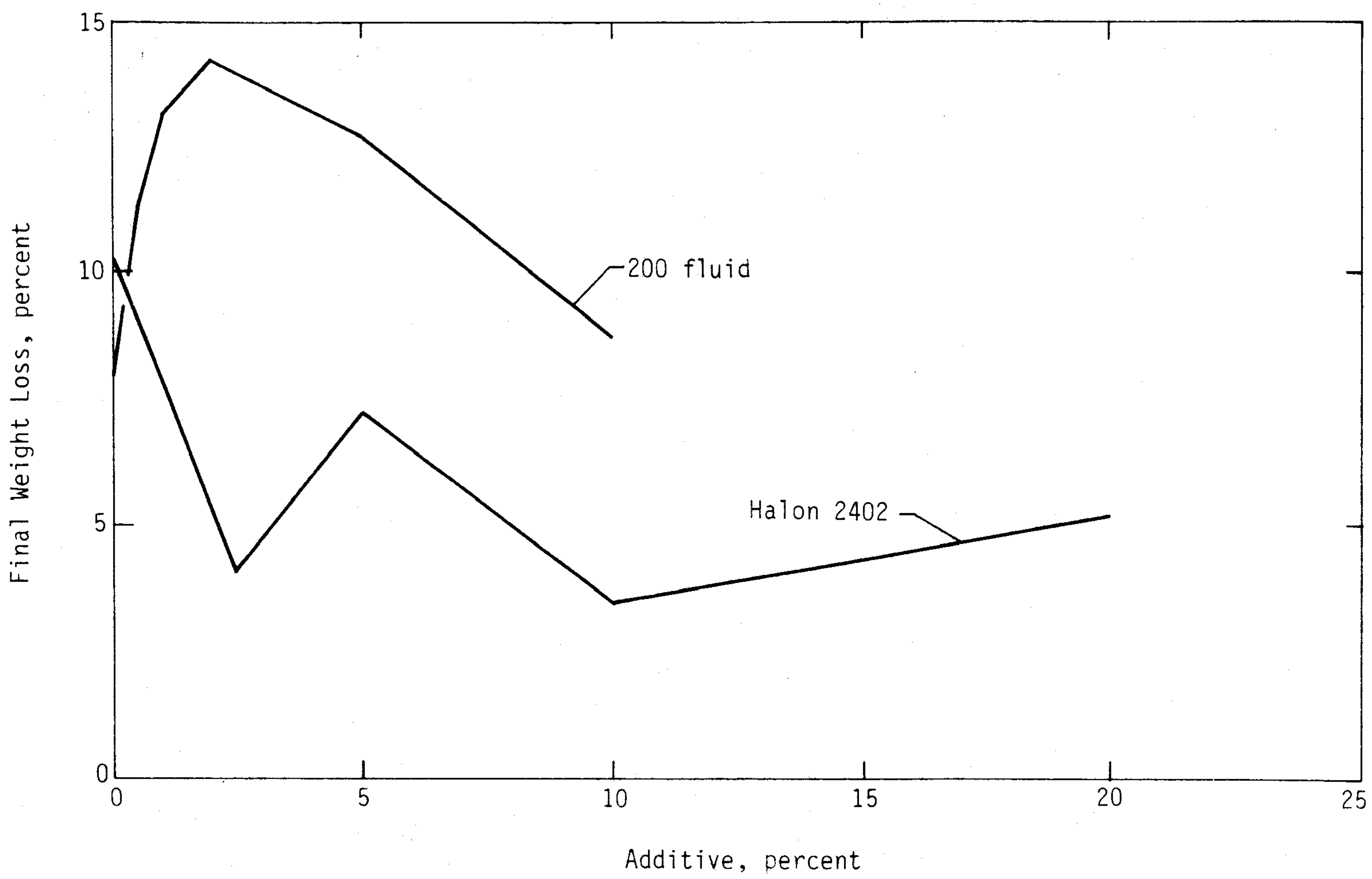


Figure 11. Weight Loss for TMB-Additive Mixtures as a Function of Additive Amount After 502 Hours of Open-Air Aging (Study 2).

used with both TMB and the reformulated agent. In these studies, ASTM test D543-67 was employed. Weight, dimension (length, thickness, width), and hardness changes were monitored for eight plastics (Delrin, polyvinylchloride [PVC], nylon, acrylic, low-density polyethylene [LDPE], high-density polyethylene [HDPE], polycarbonate, and Teflon) and for four rubber elastomers (neoprene, butyl, buna, and silicone) in contact with TMB, Halon 2402, and a mixture of 90-percent TMB and 10-percent Halon 2402. Hardness was determined by using a durometer according to ASTM Test D2240-75. All polymeric materials All polymeric materials were tested as 25.4- by 76.2-millimeter (1- by 3-inch) strips cut from nominal 3.49-millimeter (1/8-inch) thick sheet stock. Three samples of each polymer were tested with each agent. The plastics were allowed to sit for 57 days and the elastomers for 67 days. Single measurements of weight and length and multiple measurements at different locations of thickness (three locations), width (two locations), and hardness (five locations) were performed on each sample before and after aging. A separate closed container was employed on each strip tested. The results are given in Tables 9-11.

The results show that both Halon 2402 and TMB attack certain polymers. It is of interest that some polymers are affected to a significantly greater extent by the Halon, and others are affected more by the TMB. The results of the aging tests in which 90-percent TMB with 10-percent Halon 2402 was used are of greatest interest because this reformulated agent shows the most promise as a Class D extinguishant. Of the plastics, PVC, Delrin, and Teflon exhibit the smallest changes in properties and dimensions after they have been aged with TMB-Halon, PVC showing the least change. Nylon, LDPE, and HDPE were the next best. The remaining plastics (acrylic and polycarbonate) deteriorated significantly. All of the rubbers were affected by the agent. Buna and silicone rubber exhibited exceedingly large changes in dimension or appearance, or both. These compatibility results indicate that for long service life, extinguishing equipment should be designed so that contact between a Halon-modified TMB agent and any of the materials tested (with the possible exception of PVC, Delrin, and Teflon) is limited. It may prove necessary to test additional rubbers for use as gasket materials.

TABLE 9. PROPERTY CHANGES FOR POLYMERS IN CONTACT WITH TMB.[a]

Polymer	Hardness change[b]	Change, percent			
		Weight	Length	Thickness	Width
Delrin	-1.8(15)	0.83(2)	0.06(2)	1.2(6)	0.15(5)
PVC	-0.1(12)	0.00(1)	0.12(5)	-0.2(10)	0.02(18)
Nylon	3.9(10)	-0.49(1)	-0.12(1)	0.5(5)	-0.22(6)
Acrylic	0.7(9)	-5.49(13)	-0.27(2)	-4.3(4)	-0.58(3)
LDPE	-3.0(8)	1.24(2)	0.38(4)	0.5(6)	0.36(4)
HDPE	-0.3(10)	0.74(2)	0.24(4)	0.6(8)	0.18(6)
Polycarbonate	-8.5(28)	4.41(41)	0.19(5)	6.6(14)	0.92(12)
Teflon	-1.6(9)	0.06(0)	0.17(11)	1.2(6)	0.13(11)
Neoprene	7.9(9)	2.93(32)	-0.18(28)	-0.9(6)	0.11(25)
Butyl	2.5(7)	0.86(1)	0.25(8)	-0.4(4)	0.21(14)
Buna	-15.1(9)	110.04(82)	25.09(22)	30.3(8)	28.82(53)
Silicone[c]	---	---	---	---	---

[a] Average deviations of last significant digit are given in parentheses.

[b] A Type D durometer was used for the plastics and a Type A durometer for the rubber elastomers.

[c] Sample so deteriorated that changes could not be determined.

TABLE 10. PROPERTY CHANGES FOR POLYMERS IN CONTACT WITH HALON 2402.[a]

Polymer	Hardness change[b]	Change, percent			
		Weight	Length	Thickness	Width
Delrin	-0.4(8)	0.22(1)	0.01(1)	-0.5(5)	-0.07(4)
PVC	-0.2(6)	-0.02(0)	0.02(1)	0.5(10)	0.07(10)
Nylon	3.3(12)	0.12(1)	0.00(0)	0.3(5)	0.07(8)
Acrylic	0.4(9)	[c]---	[c]---	0.3(6)	-0.10(7)
LDPE	-4.2(12)	14.38(2)	1.96(5)	2.1(7)	1.65(5)
HDPE	-3.4(7)	9.15(10)	1.39(1)	1.7(5)	1.10(10)
Polycarbonate	-1.3(8)	-0.01(1)	0.03(0)	0.0(7)	0.02(6)
Teflon	-5.3(8)	3.90(136)	0.41(1)	3.2(9)	0.52(6)
Neoprene	8.9(8)	4.92(152)	-3.68(20)	-8.2(3)	-3.89(31)
Butyl	-7.0(8)	48.76(26)	3.69(3)	7.1(5)	4.49(19)
Buna	-15.4(28)	42.90(222)	1.74(18)	[d]---	2.05(12)
Silicone[e]	-2.2(7)	-3.66(11)	-1.44(8)	-3.2(4)	-1.12(9)

[a] Average deviations of last significant digit are given in parentheses.

[b] A Type D durometer was used for the plastics and a Type A durometer for the rubber elastomers.

[c] Acrylic breaks into pieces in Halon 2402.

[d] No thickness measurement was made in buna owing to pockets of Halon 2402 within the sample after it had been aged.

[e] Silicone rubber sample shrank between the time it was removed from the Halon 2402 and the time of measurement (about 24 hours later). The immediate dimensions upon removal were about 50 percent larger than the dimensions before aging.

TABLE 11. PROPERTY CHANGES FOR POLYMERS IN CONTACT WITH MIXTURE OF 90-PERCENT TMB AND 10-PERCENT HALON 2402.[a]

Polymer	Hardness change[b]	Change, percent			
		Weight	Length	Thickness	Width
Delrin	0.9(8)	0.88(2)	0.07(2)	0.8(9)	0.12(3)
PVC	0.4(6)	0.10(2)	0.06(1)	0.2(10)	0.07(7)
Nylon	4.9(13)	-0.48(3)	-0.16(1)	0.4(4)	-0.15(5)
Acrylic	0.7(9)	-4.94(131)	-0.38(1)	-6.6(5)	-0.80(3)
LDPE	-1.6(8)	3.66(2)	0.62(4)	0.7(2)	0.62(6)
HDPE	-1.3(7)	1.56(2)	0.43(4)	0.3(5)	0.25(10)
Polycarbonate	-9.2(17)	7.31(26)	0.31(6)	7.0(9)	1.03(15)
Teflon	-1.1(13)	0.21(1)	0.23(13)	0.8(7)	0.13(4)
Neoprene	6.6(8)	9.27(46)	0.18(16)	0.5(5)	0.18(42)
Butyl	1.5(10)	6.54(55)	0.60(5)	0.4(4)	0.66(25)
Buna	-17.8(9)	121.80(50)	25.86(17)	31.5(6)	29.58(30)
Silicone[c]	---	---	---	---	---

[a] Average deviations of last significant digit are given in parentheses.

[b] A Type D durometer was used for the plastics and a Type A durometer for the rubber elastomers.

[c] Sample so deteriorated that changes could not be determined.

Fire Tests

In addition to tests performed during the reformulation (Table 4), other fire tests were conducted as described in this section.

Large-Scale Tests

The following large-scale fire tests were performed during Phase II. All tests were recorded on video tape.

For the first test, a B-52 engine cowling was supported 1.5 meters (5 feet) above the ground, and one-half was loaded with approximately 45 kilograms (100 pounds) of magnesium scrap consisting of rocket fins, small structural brackets, and 3.18-millimeter (1/8-inch) sheeting. The magnesium was ignited and allowed to burn for approximately 2 minutes. Before extinguishment began, most of the pieces of scrap were at least partially burning, and magnesium had burned through the aluminum cowling in several places. Most of the fire was above the level of the fire fighters' heads. A single 9.5-liter (2.5-gallon) extinguisher containing a mixture of 90-percent TMB and 10-percent Halon 2402 was used to suppress the fire. With one-half of the extinguishing agent, the intense magnesium fire was rapidly knocked down. The rest of the agent was used to extinguish some small, flaming, indirectly accessible spots that persisted. A water spray applied after the TMB-Halon had been exhausted caused a few hot spots to react, but the water extinguished these in a short time. An attempt to reignite the magnesium after the fire had been extinguished failed. Overall, the test was very successful. The performance of the TMB-Halon mixture was impressive. A fine spray could prove to be more efficient in the indirectly accessible spaces.

A second large-scale magnesium fire test was performed to verify the capability of the reformulated agent to extinguish general-configuration magnesium fires. Approximately 90 kilograms (200 pounds) of magnesium were ignited in a mockup engine nacelle constructed from B-52 engine cowlings. The 90-percent TMB with 10-percent Halon 2402 agent, followed by a water spray, successfully extinguished the fire. Less than 19 liters (5 gallons) of agent were required.

In addition, four large-scale magnesium fire tests were conducted so that the performance of the TMB-Halon mixture and that of the current standard MET-L-X agent could be compared. For these and future large-scale tests, two 38-liter (10-gallon), wheeled chlorobromomethane (CB) extinguishers were modified to handle a TMB-Halon mixture and the MET-L-X agent. New 9-meter (30-foot) hand lines were attached, and shutoff valves and nozzles were acquired. Each fire was fueled by approximately 90 kilograms (200 pounds) of magnesium suspended 1.5 meters (5 feet) above the ground in a pair of B-52 engine cowlings. Figures 12 and 13 show the large-scale test. A prolonged preburn of

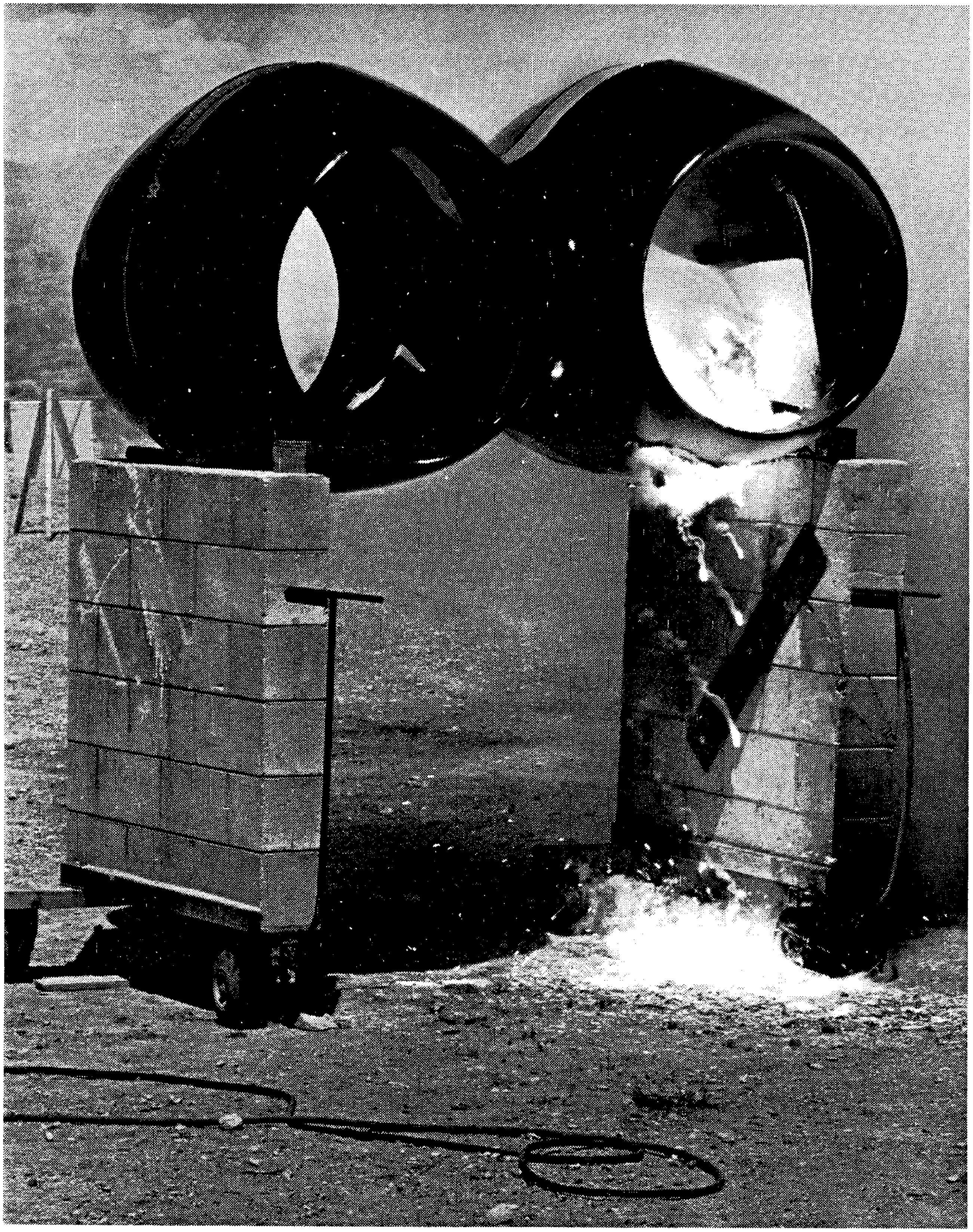


Figure 12. Large-Scale Test Apparatus.

Figure 13. Large-Scale Test Extinguishment.

20 minutes was allowed in each case. In the first test a mixture of approximately 19 liters (5 gallons) of 90 percent TMB with 10 percent Halon 2402, with a water assist, was used to combat the fire. The modified CB extinguisher was used with a much higher agent application rate (approximately 38 liters [10 gallons] per minute) than that used in any previous test. The agent was not applied in the most effective manner and was exhausted before the fire was completely extinguished. However, the agent did control the intense white magnesium fire, and no violent reaction occurred when water was applied. Prolonged water application extinguished the fire.

In the second test in this series, the modified CB extinguisher contained a total of 57 liters (15 gallons) of MET-L-X, having a mass of 68 kilograms (150 pounds). At the end of the preburn, most of the flaming suspended metal burned through the bottom of the cowlings and fell to the ground. This fire was not ideal for comparison with the first, but it should have been more easily extinguished by the MET-L-X. Again the agent was applied at a very high rate (approximately 38 liters [10 gallons] per minute), and, in this case, very little of the agent was wasted. Although the MET-L-X somewhat reduced the intensity of the fire, the metal continued to burn vigorously. Application of water seriously aggravated the fire. At this point, 9.5 liters (2.5 gallons) of TMB was applied to the fire. The fire was still not extinguished, but it was now possible to apply water, without causing a violent reaction, to extinguish the fire by cooling it.

In the last two tests of this series of four, MET-L-X and 90-percent TMB with 10-percent Halon 2402 were applied to nearly identical fires. In the third test, an extinguishant of 112 kilograms (247 pounds) of MET-L-X was used in an attempt to control the metal fire. The application of water after the MET-L-X had been exhausted produced more violent reactions than had the TMB-Halon mixture but it eventually extinguished the fire. During the last test, the fire was controlled by an application of 34.5 kilograms (76 pounds) of TMB-Halon. Water was then used to completely extinguish the fire.

Modified/Medium-Scale Tests

During Phase II, a new medium-scale test was designed. The purpose was to determine the minimum amounts of MET-L-X, TMB, and TMB-Halon required for extinguishing magnesium fires of varying sizes. A 0.6- by 1.2-meter (2- by 4-foot) welded steel pan, 102 millimeters (4 inches) deep, was used as a platform for the fires. The platform was supported by four cylindrical concrete blocks, 559 millimeters (22 inches) long by 305 millimeters (12 inches) in diameter (Figure 14), and a series of stacked concrete cinderblocks. The platform was approximately 610 millimeters (24 inches) above the ground. Two torches, mounted near the platform, were pointed toward the center of the pan (Figure 15). The magnesium was cut into blocks of about 500 grams (1 pound) each. One, two, or three blocks were used per test. The blocks were stacked in an irregular pattern to simulate the configuration of a concealed or confined fire. All tests were recorded on videotape. In addition, test personnel recorded their visual observations. The test results are shown in Table 12.

TABLE 12. RESULTS OF MODIFIED MEDIUM-SCALE FIRE TESTS.

Agent	Fire size, blocks of Mg	Agent flowrate, g/s	Agent quantity, g	Average deviation in agent quantity for 3 tests, g
TMB-Halon	2	36	1230	201
TMB-Halon	2	94	769	152
TMB-Halon	3	82	1069	129
TMB-Halon	1	79	603	146
TMB	2	73	1304	35
MET-L-X	2	75	1952	635

The results indicate that for a fire of this size, a higher flow rate (95 g/s versus 36 g/s) gives slightly better extinguishment. They also indicate that TMB-Halon is superior to TMB, and TMB is superior to MET-L-X.

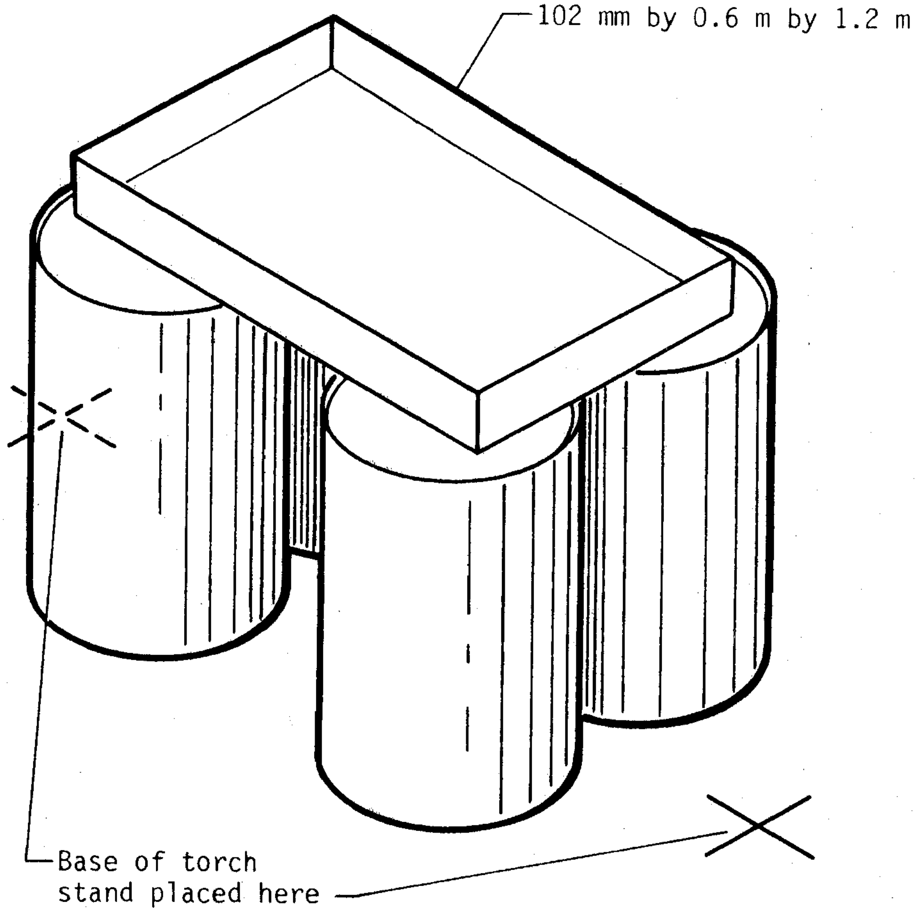


Figure 14. Modified Medium-Scale Magnesium Fire Test Apparatus.

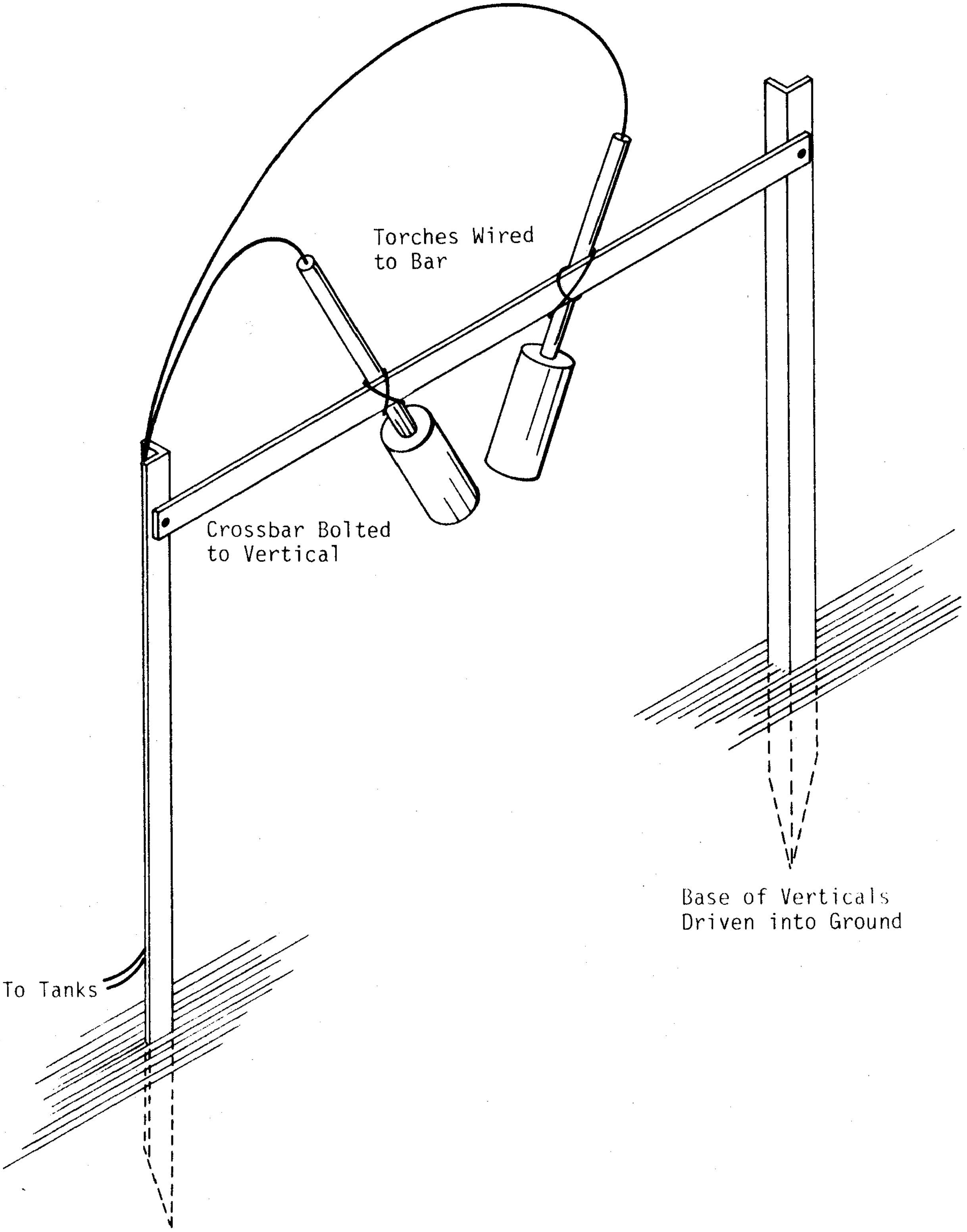


Figure 15. Torch Arrangement for Modified Medium-Scale Test.

NEW AGENT

Criteria

Two features unique to metal (Class D) fires complicate the task of developing an effective extinguishing agent (Reference 9). First, the metal fuel is highly reducing; second, the fuel is hot.

In Class D fires, both a strong oxidizing agent (oxygen) and a strong reducing agent (metal) are present. Owing to this combination, fire suppression agents that can be either oxidized or reduced may, and probably will, give a significant secondary reaction. For example, extinguishing agents such as carbon dioxide and water, which are highly effective for most other types of fires, not only fail to extinguish magnesium fires but actually enhance combustion because of their reducibility. Water is violently reduced by burning magnesium, forming hydrogen gas (which is also combustible); carbon dioxide is reduced to carbon. On the other hand, if one chooses an agent already in a reduced form, a secondary fire can occur as that agent is oxidized by the oxygen present. For example, hydrocarbons can often extinguish a magnesium fire, at least temporarily, without reacting violently with the magnesium, but such agents usually create a secondary fire. In this case, one trades a Class D fire for a Class B fire. The problem with agent flammability is increased by the high burning temperature of magnesium (the flame temperature is around 3000°C). As a result of the potential for the occurrence of either oxidation or reduction of the agent, agent reactivity is an important consideration. Yet exceedingly few materials are oxidizable or reducible at the temperature of burning magnesium.

A secondary problem with metal fires is that the fuel is hot. Consequently, certain extinguishment methods that might function for Class A or Class B fires, where the bulk of the fuel is usually at a much lower temperature than that of the fire, fail when they are used on Class D fires. For example, a Class D fire normally cannot be blown out because, as a result of the high thermal conductivity of the metal, much or all of the fuel may be at or near the ignition temperature. In this case, the removal of free radicals does not terminate the combustion reaction, which continues as long as the temperature is sufficiently high. Similarly, because of this large thermal reservoir, the use of cooling to extinguish metal fires is relatively ineffective. Most agents simply do not possess enough cooling capacity that cooling can be employed as the only means of suppressing metal fires. The most troublesome effect of the large thermal reservoir provided by the hot fuel, however, is the potential for reignition. Laboratory work indicates that if reignition can occur, it will. Many agents will temporarily suppress a metal fire, but reignition often occurs. This work indicates that the only effective way to prevent reignition is to separate the hot metal fuel from oxygen, which can be done by inerting the surface. One way to do this is to add a coating material to the magnesium; however, other methods are theoretically available as described in the next subsection. Thus, the second important property that a Class D fire extinguishant must have is surface-inerting ability.

A number of other characteristics are desirable. The Class D agent should be capable of reaching indirectly accessible areas of a fire and should have a good throw range (applicability). The agent must be noncorrosive to containers, extinguishing equipment, and aircraft (compatibility). It must not have a high toxicity, and it should present no intolerable storage or handling problems (stability). Above all, it must be effective. It must extinguish metal fires and keep them extinguished. Only by testing (and this must include large-scale metal fire tests) can effectiveness be determined. The properties that must be considered, then, for a Class D fire-fighting agent are

Reactivity
Toxicity
Cooling ability
Economics
Effectiveness
Surface-inerting ability
Applicability (range, ease, coverage)
Stability
Compatibility with other materials

Surface Inerting

The agent TMB exhibits excellent surface-inerting properties and thus does an excellent job of preventing reignition. Primarily for this reason, TMB is more effective than MET-L-X. It has been generally believed that TMB suppresses magnesium fires by coating the fuel with boron trioxide,

B_2O_3 (Reference 6). Thermodynamic considerations, however, show that liquid boron trioxide is unstable in the presence of hot magnesium or magnesium oxide, as indicated by the free energy changes (ΔG°) calculated from reported data (Reference 10) for the formation of boron from either solid (s) magnesium or liquid (ℓ) magnesium at 1000 K (the temperature of burning magnesium is about 1300 K [Reference 3]).

	ΔG°, kcal/mol	
$B_2O_3(\ell) + 3Mg(s) \rightarrow 3MgO(s) + 2B(s)$	-113	(4)
$B_2O_3(\ell) + 3Mg(\ell) \rightarrow 3MgO(s) + 2B(s)$	-111	(5)

A negative free-energy change is the sole criterion for a spontaneous reaction. Of course, thermodynamic considerations of this type do not ensure that the reaction will be sufficiently fast to occur on a reasonable time scale (the life of the magnesium fire in this case); however, the high temperatures involved and the fact that boron trioxide is liquid under these conditions (melting point = 460°C) give reasonable assurance that the reactions will proceed. In fact, such reactions are the foundation of the "Moissan process" for the synthesis of elemental boron (Reference 11).

Moreover, after its formation, the boron is expected to react further with magnesium to form various magnesium borides, MgB_2, MgB_4, MgB_6, or MgB_{12} (References 12 and 13). At 1000 K, the free energy of formation of MgB_2 from $Mg(\ell)$ and B(s) is -19.2 kcal/mol, and the reaction is therefore favorable. Magnesium oxide (which will be present on the surface) can also react with boron trioxide to form various magnesium borates. Thus, relative to solid magnesium oxide and liquid boron trioxide, the following free energy changes hold (Reference 14):

	ΔG°, kcal/mol	
$3MgO(s) + B_2O_3(\ell) \rightarrow Mg_3B_2O_6(s)$	-117	(6)
$2MgO(s) + B_2O_3(\ell) \rightarrow Mg_2B_2O_5(s)$	-131	(7)
$MgO(s) + 2B_2O_3(\ell) \rightarrow MgB_4O_7(s)$	-105	(8)

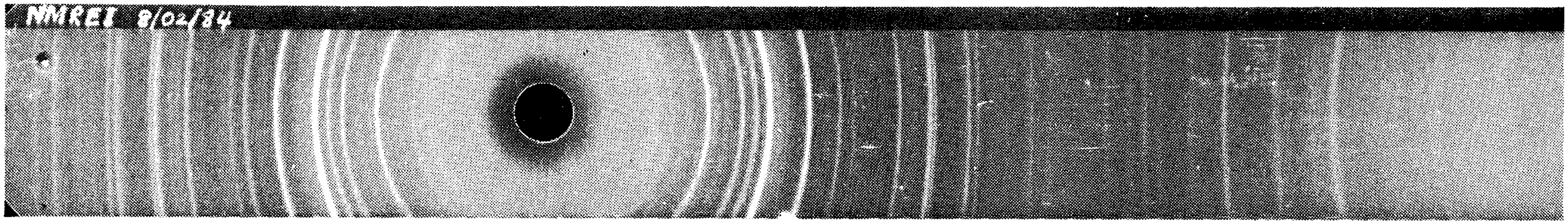
A large number of other products, some of them suboxides or nonstoichiometric compounds, can be formed in reactions of boron trioxide with magnesium (Reference 15).

Two small pieces of magnesium were ignited to characterize the surface-inerting materials obtained with TMB. One piece was extinguished with water and the other with TMB. The surfaces of both pieces were scraped, and X-ray powder patterns were obtained (Figure 16). By comparing patterns of known compounds with those obtained from the surfaces (a mixture), one can identify the compounds and the specific solid phases present. This work is continuing, and the results thus far do show the presence of free boron. Interestingly enough, boron trioxide is not present; however, its absence is not surprising. Boron trioxide is highly hygroscopic and rapidly picks up water to form boric acid, which is found.

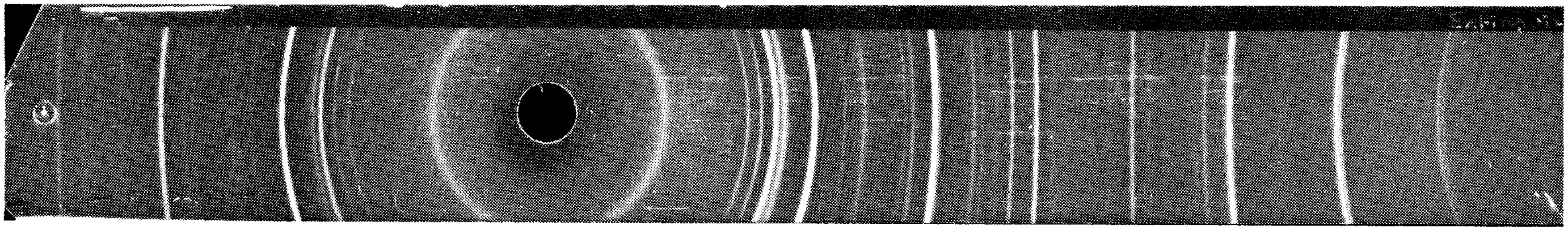
New Agent Concepts

A number of possible methods exist for achieving surface inertion of metal fires. Indeed, the work thus far suggests that a simple coating action may not be the mode of action for TMB. Like boron trioxide from TMB, other oxides could form not only crusting materials but also materials formed from reaction with magnesium. For example, compounds giving silicates could give free silicon, magnesium silicides, and magnesium silicates (in the same way that boron, borides, and borates may be formed with TMB). The reactions are all highly favorable. Similarly, phosphate compounds, such as phosphate esters, could give phosphorus (not desirable), phosphides, and phosphates. Phosphate esters are known to extinguish metal fires (Reference 16); however, relatively little work has been done on these compounds. Silicate esters and, in particular, phosphate esters are generally more resistant to hydrolysis than are borate esters (such as TMB).

Phase III will also examine potential coating materials. Boron amines could give a boron nitride polymeric coating, and organosilanes could coat with silicon carbide. Indeed, the formation of silicon carbide in such a reaction has been reported (Reference 17). The ability of certain metal alkoxides and organometallic sols or gels to form ceramics when they are heated suggests a highly promising method of forming an inert coating (Reference 18).



Extinguished with TMB



Extinguished with water

Figure 16. X-Ray Powder Patterns for Materials on Surface of Extinguished Magnesium.

A special laboratory-scale magnesium fire test has been designed for the rapid screening of some of these compounds (Figure 17). This test does not enable one to determine which compounds will be good agents, but it does permit one to discard certain compounds as being too reactive or failing to inhibit reignition. The test has been used to screen some polysiloxanes and phosphate esters. Surprisingly, polysiloxanes extinguish the flame but do not inhibit reignition. Apparently the silicon dioxide formed does not coat the surface well. Molten silicon dioxide has an exceedingly high surface tension.

PLAN FOR PHASES III AND IV

In Phase III, new agents will continue to be developed and tested for extinguishing fires fueled by a combination of metals. Tests will be designed for aluminum, titanium, magnesium, and combinations thereof. Known agents, including those studied in Phases I and II, will be screened in laboratory-scale tests. New potential fire-suppression agents will also be prepared or otherwise obtained and screened. Agents showing superior suppression qualities will be tested in medium-scale tests, and those performing well will be tested in large-scale metal fire tests. Any agent selected as a potential final candidate will be carefully compared with modified TMB.

In Phase IV, large-scale testing will be performed on the agent selected. A delivery system will be designed and a prototype system developed. The final tests will involve all aircraft metals that have caused fire problems. A compound fire situation, involving jet fuel and burning metal, will be used in the full-scale tests.

PHASE II CONCLUSIONS AND RECOMMENDATIONS

Of the materials tested, TMB-based extinguishants are clearly the agents of choice for combating magnesium fires. Not only does TMB extinguish such fires but, because of its superior surface-inerting properties, it also prevents reignition. The addition of Halon 2402 to TMB at the 10-percent by volume level significantly improves the overall performance: viscosity is lowered, aging changes are reduced, flammability is decreased, and handling

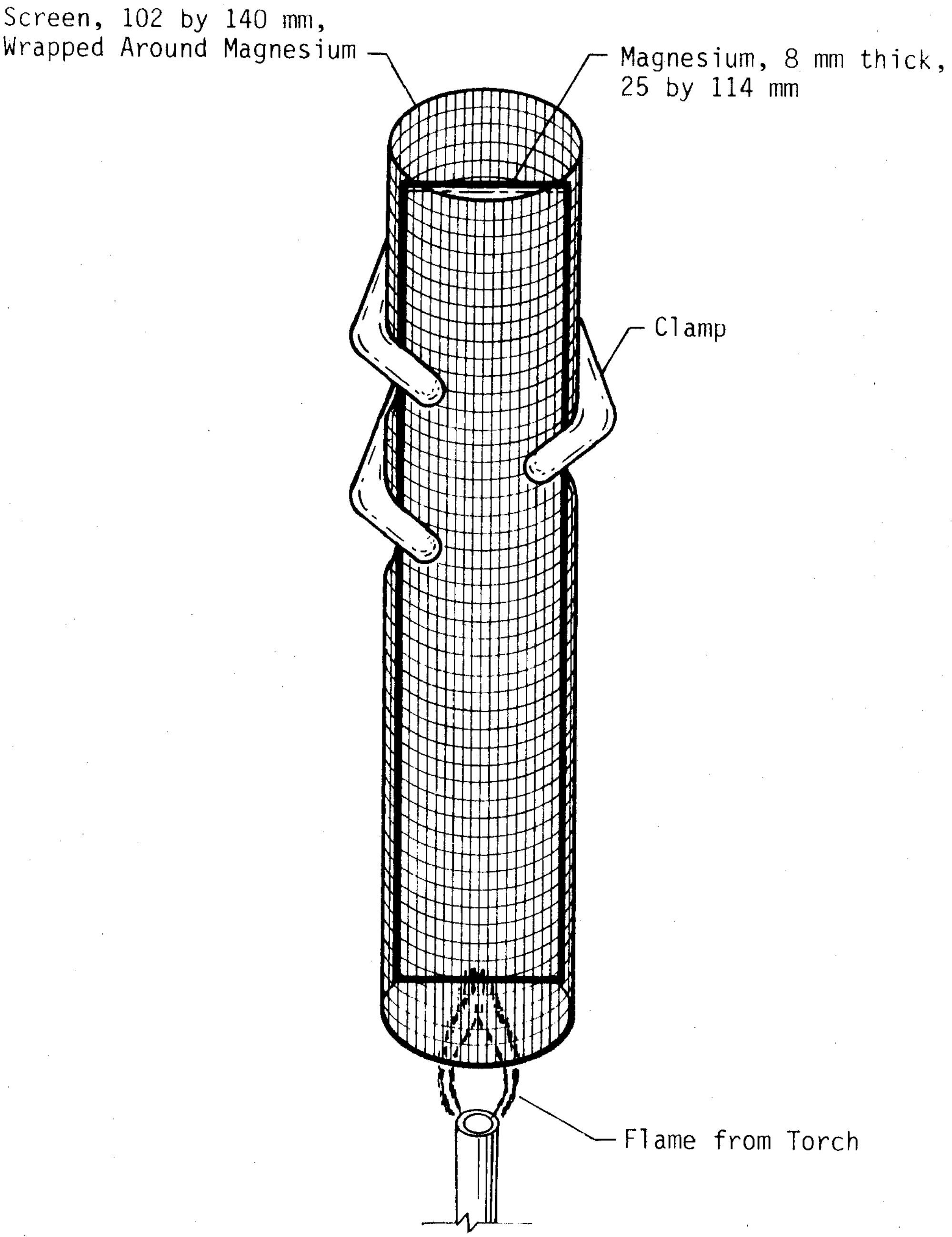


Figure 17. Laboratory-Scale Magnesium Fire Test.

properties are improved. A qualitative comparison of Halon-modified TMB and MET-L-X, the current Air Force Class D firefighting agent, is presented in Table 13. The most important characteristic listed in this table is "effectiveness." Modified TMB is more effective than MET-L-X for suppressing magnesium fires.

Although the TMB-Halon agent has been shown to be superior to other agents tested, it is less than ideal. Flammability, handling, and hydrolysis problems have not been solved. Moreover, in large-scale tests, complete extinguishment does not always occur. Consequently, the development of a new formulation must continue in Phase III.

The investigations show that only large-scale tests can provide a realistic evaluation of an agent. These tests also indicate that, if either TMB-based agents or MET-L-X is to be used effectively, firefighters must be trained on large metal fires.

TABLE 13. COMPARISON OF HALON-MODIFIED TMB AND MET-L-X.

Criterion	Modified TMB	MET-L-X
Compatibility with other materials	**	****
Toxicity	***	****
Stability	**	****
Reactivity	***	****
Applicability (range, ease, coverage)	***	**
Cooling ability	*	**
Surface-inerting ability	****	**
Economics	**	***
Effectiveness	***	**

Notes: **** = excellent; *** = good; ** = fair; * = poor.

SECTION IV

PHASE III--COMBINATION OF METALS

TECHNICAL REQUIREMENTS FOR PHASE III

Laboratory-scale combustion tests involving magnesium, aluminum, and/or titanium shall be established and used to screen both new potential and previously studied Class D firefighting agents. Medium-scale and large-scale tests shall be used to further examine agents showing superior extinguishment in small-scale tests. The large-scale tests shall be thoroughly documented. Information on appropriate delivery systems, suspected or known breakdown products, toxicity and environmental properties reported for the agent, stability, corrosiveness, and economics shall be provided.

Phases I and II, accomplished under Contract No. F29601-81-C-0013, identified several agents which extinguished metal fires; however, only one agent, TMB, could effectively extinguish such fires in both horizontal and vertical configurations (References 5 and 19). Other agents tested proved effective only on horizontal magnesium fires. TMB exhibits some adverse properties--primarily its flammability and poor aging characteristics. The Phase II effort revealed that the addition of Halons greatly decreases the flammability and improves certain other characteristics. In Phase III, Halon-modified TMB will continue to be tested, old agents will be retested, and new agents will be examined, using fires which include titanium and aluminum fuels in addition to magnesium.

NOMENCLATURE

Much of the work reported in the remainder of this document covers mixtures of TMB with halons. Present nomenclature--for example, "90 percent TMB with 10 percent Halon 2402, by volume"--is cumbersome. In the following material and in future reports from this laboratory, the designation "Boralon-1" and "Boralon-2" will be used to name TMB/Halon 1211 and TMB/Halon 2402 mixtures, respectively. The composition will be added as, e.g., 10 V or 20 W to denote the volume (V) or weight (W) percent of halon in the mixture. Thus, "Boralon-1-30V" is the designation for a mixture containing 30 percent Halon 1211 and 70 percent TMB, by volume. It is important to distinguish carefully between weight and volume bases for the TMB/Halon mixtures. Due to the large densities of most halons, the differences between weight and volume percentages are significant. The amount of Halon 2402 in Boralon-2-10V is 10 percent by volume but 16 percent by weight.

LABORATORY TESTING

Extinguishment Tests

Three series of extinguishment tests were designed for laboratory screening of potential agents. Two series ("strip tests") used .79- and 1.59-millimeter (1/32- and/or 1/16-inch) thick metal, cut 38.1 by 127 millimeters (1 1/2 by 5 inches), clamped on a ring stand in a fume hood. One series employed three strips of magnesium; the other used mixed metals (normally one strip each of magnesium, aluminum, and titanium). In the magnesium strip tests, the three magnesium strips were bent into an arc of approximately 120 degrees (Figure 18). The test samples for the mixed-metal tests were left unbent. In a third test, blocks of metals, 25.4 to 38.1 millimeters (1 to 1 1/2 inches) on a side, were used. Test samples comprised only of magnesium were ignited with a propane torch. Other samples were ignited with an oxyacetylene torch. Titanium and aluminum exhibited synergistic effects. When in contact, these two metals burned much more intensively than did the metals by themselves. Aluminum would not burn by itself, and titanium burned only moderately well by itself in block form and poorly in sheet form.

Solid agents were applied to the fire with a sandblasting apparatus. Liquids were applied with either the sandblaster or with a hand-operated sprayer. The agent container in the delivery system was weighed before and after application to determine the amount of agent used. The time to first extinguishment was also recorded. If reignition occurred, this fact was noted. The agent action, formation of crust, appearance of the metals surface, and other features associated with agent action were noted. Tests were documented by video. Laboratory personnel wore respirators, gloves, caps, UV radiation goggles, and other protective clothing.

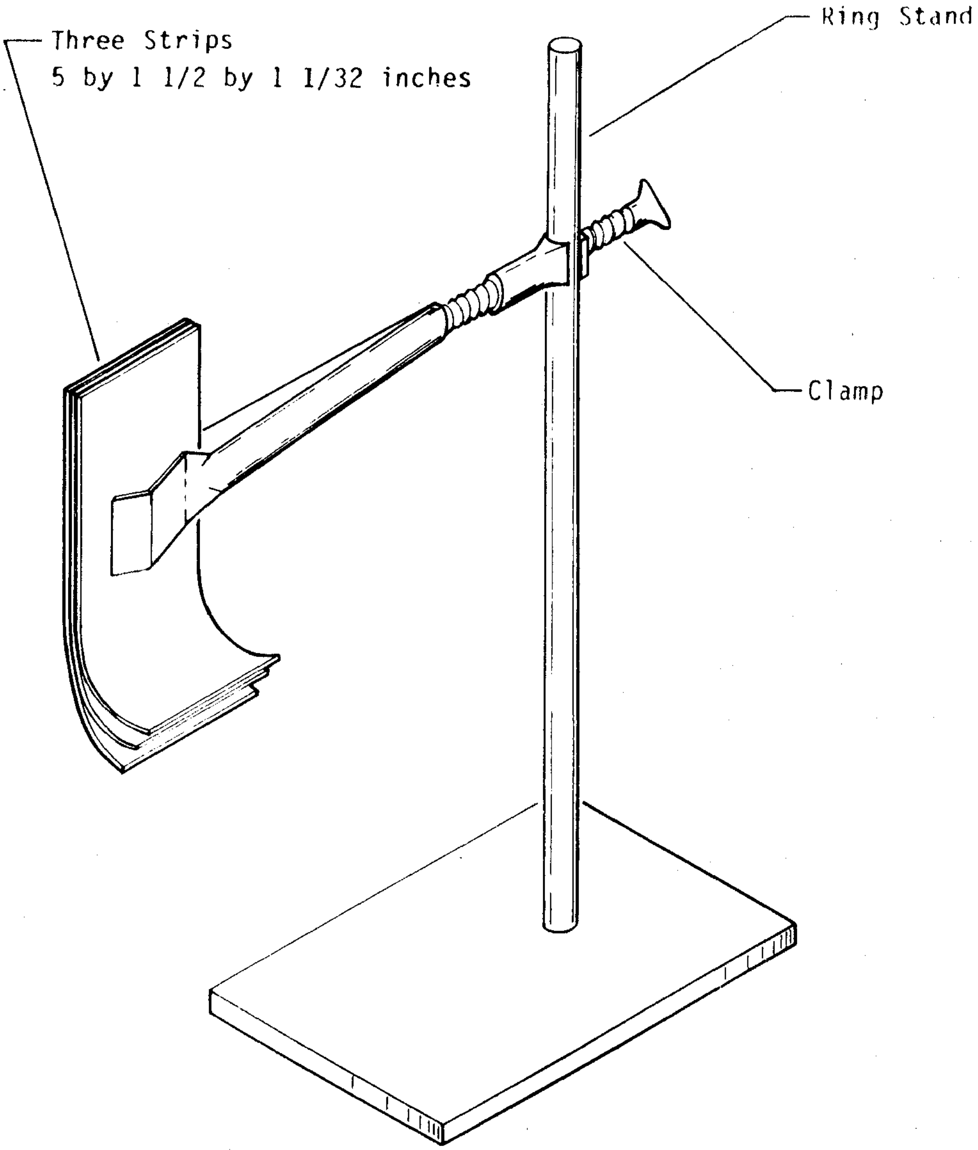


Figure 18. Magnesium Extinguishment Strip Test.

Sixty-four agents (Table 14) were tested in laboratory-scale tests, in many cases, several times. The data from the magnesium strip tests are presented in Appendix C. Although block tests and strip tests involving metals other than magnesium provided observations and results important to the overall evaluation, the data were scattered and were difficult to reproduce. For these reasons, quantitative data on these latter tests are not given. In general, agents appear best on laboratory- and small-scale tests and worse with larger amounts of fuel. Laboratory-scale tests are useful for screening agents to determine which will not work and which react with heat and hot metal (large secondary fire, violent reactions, unpleasant gases, etc.).

Calcium chloride, lithium chloride, ammonium chloride, and Borester 20 (a nitrogen/boron organic manufactured by U.S. Borax) proved difficult or impossible to deliver, because of their hygroscopicity. The delivery nozzle tended to clog with these agents. Silica gel was added; however, in most cases this addition harmed the extinguishment characteristics. Some other solid agents--boron, hydrated boric acid, hydrated sodium carbonate--also could not be delivered due to nozzle clog. Exceedingly limited tests of boron were run with a hand application. These tests indicated that boron was a poor extinguishing agent and no further work was done to spray this material. Triethylphosphite smelled so badly that only a partial evaluation of this agent was attempted. This work, however, indicated that a phosphorus-containing ester is much poorer than boron compounds in extinguishing metal fires.

A number of solids had questionable extinguishment ability, as noted in Table 14 and Appendix C. These agents appeared to quench the white fire which is characteristic of burning magnesium, but the residue continued to glow. When examined, the residue exhibited no free magnesium metal.

Although a number of solid agents gave acceptable extinguishment in these small-scale tests, none were so good that they could be seriously considered. Because earlier testing had shown the superiority of liquid agents, a solid agent would have to give outstanding extinguishment. No liquid tested was as good as TMB in these tests.

Several liquids burned sufficiently to ignite the magnesium. All three silicone oils tested exhibited this behavior. Surprisingly, triethylborate,

TABLE 14. AGENTS EVALUATED IN LABORATORY-SCALE EXTINGUISHMENT TESTS.

Extinguished magnesium fire

MET-L-X
Monex
Flarex
Borax
Iron powder
Boralon-2
Bentonite
TMB
Glass flake
TEC powder

Foundry Flux 230
Generic foundry flux
Dow Corning 200 silicone oil, 20 cSt
Ammonium phosphate
Ammonium chloride
Saran Resin F120
Ammonium chloride/silica gel
Diisodecylphthalate[a]
Ethyleneglycol/boric acid[a]
Dow Corning 510 silicone oil[a]
Dow Corning 200 silicone oil, 5 cSt[a]
Bromochloromethane/diisodecylphthalate

Sodium borate/PVC[a]
Dolomite
Polyvinyl chloride
Paraffin oil
Calcium chloride
Triethylborate[a]
Copper powder
Triethylborate
Lithium chloride
Boric acid, anhydrous
Saran Resin F220

Questionable extinguishment

Feldspar
Casein
Sand
LITH-X[a]

Borester 20/silica gel
Ammonium chloride/silica gel
Lithium chloride/silica gel
Calcium chloride/silica gel
Anhydrous sodium carbonate

Lithium fluoride
Glass powder (200 mesh)[a]
G-1 Powder (200 mesh)
Sodium borate[a]

[a] Metal reignited.

TABLE 14. AGENTS EVALUATED IN LABORATORY-SCALE EXTINGUISHMENT TESTS (CONCLUDED).

No extinguishment		
Talc	Triethylphosphite	Magnesium carbonate
Na-X	Borester 20/silica gel	Sodium chloride
Perlite	Glass beads	Magnesium oxide
Sucrose	Casein/magnesium carbonate/talc	Vermiculite
Could not apply agent[b]		
Boron	Hydrated sodium carbonate	Borester 20
Sandia foam[c]	Hydrated boric acid	TMB/triethylphosphite

[b] Could not apply agent (flow problem).

[c] Special silicate/carbon dioxide foam developed by Sandia National Laboratories for security purposes.

which, like TMB, is a borate ester, had a secondary fire sufficiently large to ignite magnesium metal several times. Similar reignition by TMB has never been observed. This behavior is probably due to the lower ratio of hydrocarbon groups to boron in TMB. Each boron atom in TMB is attached to only one carbon atom, while each boron atom in triethylborate (and most other borate esters) is connected to three carbon atoms.

Chemistry

In Phase II, a number of unusual property improvements were observed in TMB when Halon 2402 was added. Laboratory studies were performed to explain the observed improvements in hopes of increasing the agent performance. In addition, information was collected on TMB containing Halon 1211, a mixture indicated by field testing (see below) to give good extinguishment.

Flammability

Phase II studies showed that the addition of Halon 2402 significantly decreases the flammability of TMB. This action is expected to be only temporary when mixture exposure to air causes halon to be lost. This flammability change was quantified with a modified Cleveland open-cup fire point test (Reference 20). Normally, in the Cleveland open-cup test, the temperature is increased until the fire point (the time at which a flame is sustained for 5 seconds) is observed. In the present case, however, the temperature was permitted to remain constant and the elapsed time at which the surface of the TMB/halon mixture sustained a flame was recorded. Two mixtures, Boralon-2-10V and Boralon-1-10V, were tested. The results are presented in Table 15 and are shown graphically in Figure 19.

TABLE 15. ELAPSED TIMES TO FIRE POINTS AS A FUNCTION OF TEMPERATURE FOR TMB/HALON MIXTURES.

Agent	Time, min			
	25°C	30°C	40°C	50°C
Boralon-1-10V	26, 23	18, 23	23, 20	17
Boralon-2-10V	36	26	13	11

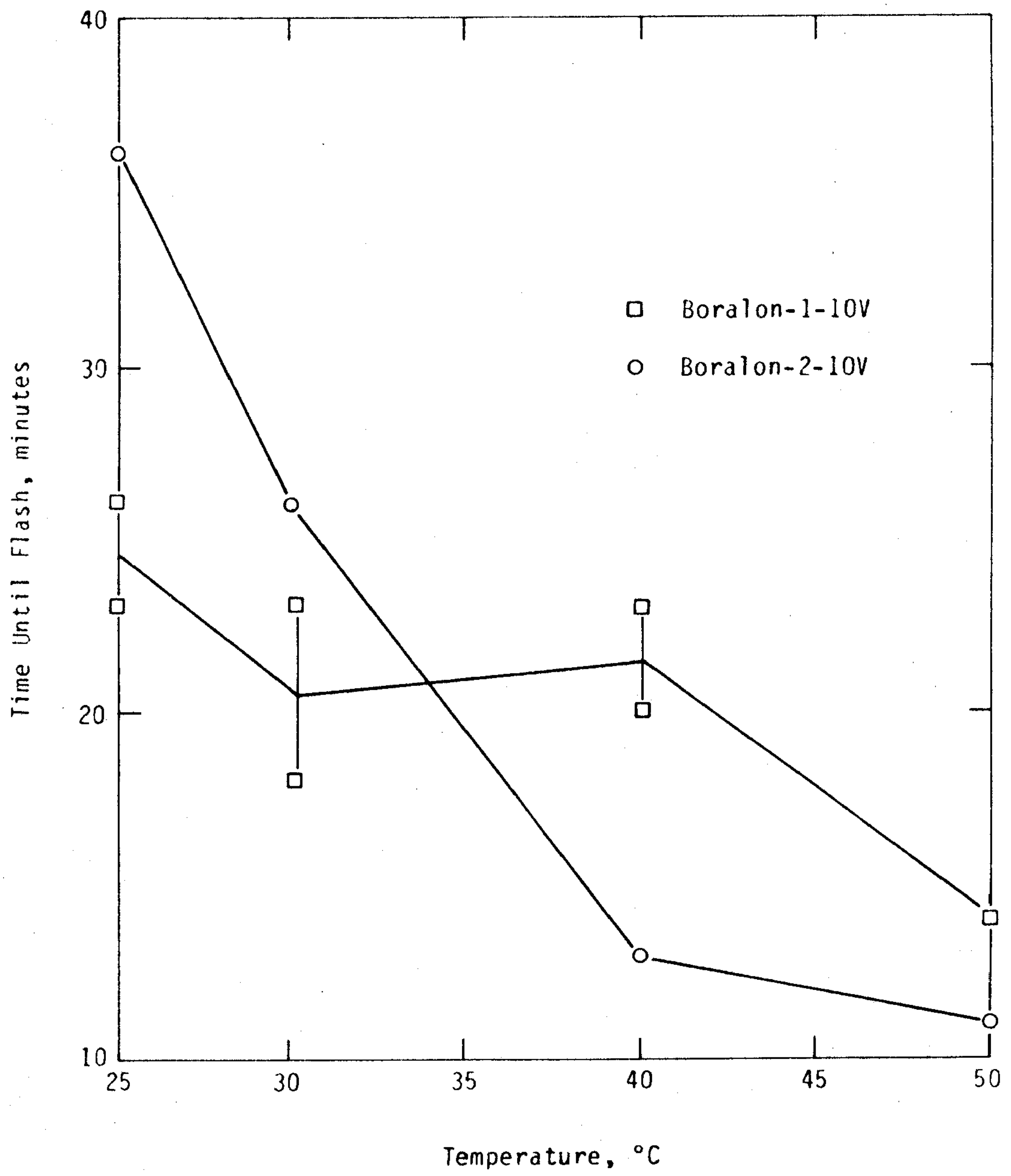


Figure 19. Elapsed Time to Fire Point as a Function of Temperature for TMB/Halon Mixtures.

As expected, Halon 2402 eliminates TMB flammability longer than does Halon 1211. Halon 2402 has a significantly lower vapor pressure at 25°C (351 torr, 0.462 atmosphere, Reference 8) than does Halon 1211 (2070 torr, 2.72 atmospheres, Reference 21) and is not lost as fast from the mixture. At higher temperatures, the difference between the TMB flammability inerting ability of the two halons decreases and above 35°C, Halon 1211 actually inerts TMB for a longer time than does Halon 2402. Note that the TMB/halon mixtures were not stirred during the flammability tests. Halon need only be lost from the surface layer in order for the liquid to ignite. When stirred, the mixture is nonflammable for a much longer time.

Viscosity

As TMB ages in an open container, a significant increase in viscosity occurs (Reference 19). This undesirable viscosity increase is apparently caused by two processes. First, hydrolysis reactions between the TMB and atmospheric moisture form boric acid and methanol (Reference 6). The excess boric acid causes polymerization, which increases the viscosity. Laboratory experiments which showed the polymerization of TMB in the presence of boron trioxide (B_2O_3, the anhydride of boric acid) were performed. The addition of boron trioxide caused the TMB to increase in viscosity and to become a solid when sufficiently large amounts were added. This increase in viscosity with boron trioxide has been noted by others (Reference 6). The second cause of viscosity increase is the loss of volatile materials. The principal volatile material which is lost is apparently trimethylborate, as determined by mass spectrometry (see below).

Mixtures of TMB/halon were allowed to sit in beakers in a constant temperature water bath at 30°C. The atmosphere above the material was at a relative humidity of 30 to 60 percent. The viscosities were measured approximately once a day on a Brookfield Model LVTD viscometer. The viscosities recorded on the first day were measured at 21°C to avoid changes from loss of halon and volatiles during the warmup period. The remaining viscosity readings were recorded at 30°C. The data collected are presented in Table 16 and

TABLE 16. VISCOSITIES OF TMB/HALON MIXTURES AS A FUNCTION OF OPEN-AIR AGING TIMES.[a]

Material	Viscosity, cP								
	0 day	1 day	2 day	3 day	6 day	7 day	8 day	9 day	10 day
TMB (control)	29	330	297	328	314	332	326	360	370
Boralon-2-5V	23	90	74	106	76	90	220	191	204
Boralon-2-10V	19	26	32	34	22	28	30	34	42
Boralon-2-15V	16	17	18	16	16	18	20	20	20
Boralon-2-20V	15	14	17	14	13	16	14	20	20
Boralon-1-5V	24	210	286	228	230	240	246	238	322
Boralon-1-10V	21	30	36	56	119	131	130	128	170
Boralon-1-20V	17	99	73	76	97	222	214	212	266
Boralon-1-30V	14	100	116	100	88	98	255	257	320

[a] All viscosity measurements were taken at 30°C except for those taken on the first day, which were recorded at 21°C.

are graphed in Figure 20. Readings were taken at approximately the same time each day. The deviations from smooth curves may be caused by temperature variations; however, every attempt was made to maintain a constant temperature of 30°C for both the aging and the measurements. Day-to-day instrument variation may also have affected the viscosity measurements. The initial viscosity of TMB at 21°C of 29 centipoises is a little higher than that reported at this temperature. The kinematic viscosity reported is 17 centistokes (Reference 2), which can be converted to centipoises by multiplication with the density of approximately 1.22 grams/cubic centimeter (Reference 22). This conversion gives a reported viscosity of 21 centipoises. Note, however, that at 24°C, a viscosity of 25.5 centipoises was determined in the earlier studies (Reference 19). This value will increase with a temperature change. Thus, the viscosities determined in these studies are a little higher than those reported elsewhere. The viscosity will probably vary, depending on the batch and on the history (handling, exposure to air).

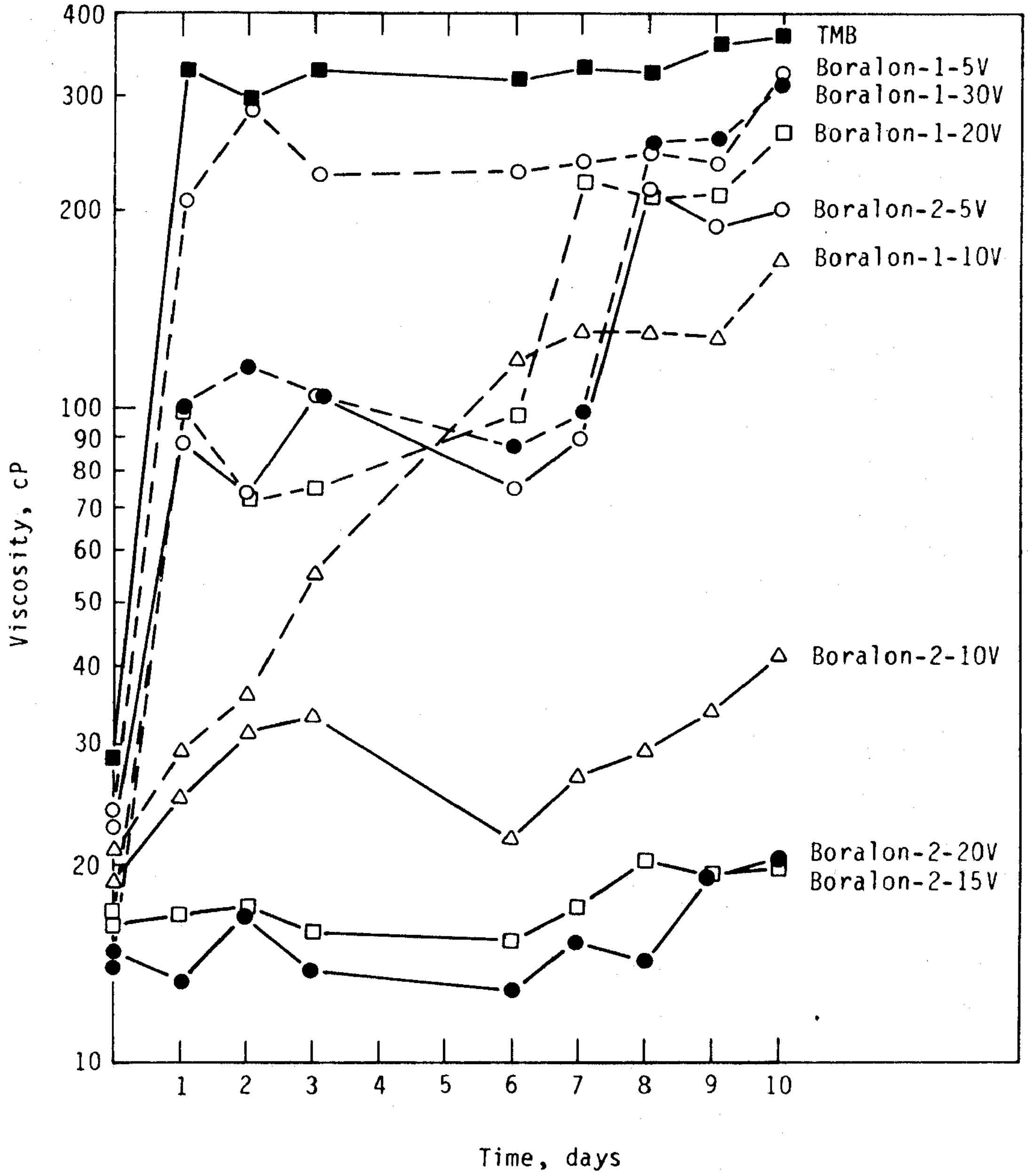


Figure 20. Viscosity of TMB/Halon Mixtures as a Function of Time for Open-Air Aging.

The addition of either Halon 2402 or Halon 1211 to TMB causes a significant decrease in the initial viscosity. The viscosities measured on day one at 21°C are shown as a function of halon concentration in Figure 21. These data can be fit with the expressions shown in Equations (9) and (10), where V is the viscosity in centipoises and P is the percent by volume of halon in the mixture. Although the viscosity of liquid Halon 2402 (0.72 cP at 25°C, Reference 8) is higher than that of liquid Halon 1211 under the same conditions (0.34 cP at 25°, Reference 21), the viscosity lowering by addition of Halon 2402 is at least as great as that affected by the addition of Halon 1211. Note, however, that viscosities of liquid mixtures are not normally linear functions of the viscosities of the components.

Boralon-1: $$V = 28.6 - 0.86\ P + 0.013\ P^2 \tag{9}$$

Boralon-2: $$V = 28.9 - 1.29\ P + 0.03\ P^2 \tag{10}$$

The viscosity of TMB increases rapidly with aging and then reaches a plateau. Those chemical changes effecting the viscosity increase are caused by reactions occurring very rapidly at the beginning of the open-air aging. The viscosity changes seen in this experiment are much larger than those seen in Phase II (Reference 19). In the present study, beakers containing the TMB/halon mixtures were kept in a water bath; therefore, the humidity (and hydrolysis) may have been much greater than in the previous studies. The earlier work concluded that hydrolysis, rather than loss of volatiles, was the major pathway for viscosity increases.

The addition of either Halon 1211 or Halon 2402 to TMB significantly decreases the effect of aging on viscosity with Halon 2402 having the greater action. Halon 1211 is lost faster than Halon 2402 from TMB/Halon mixtures and would not be expected to be as effective in maintaining the viscosity. As increasing amounts of halon are added, the action of the halon on viscosity maintenance decreases; at high halon concentrations, there is indication of a reversal. This is particularly obvious in the case of Halon 1211. A trend indicating an optimal concentration for the effect of Halon 2402 on viscosity was also seen in Phase II (Reference 19).

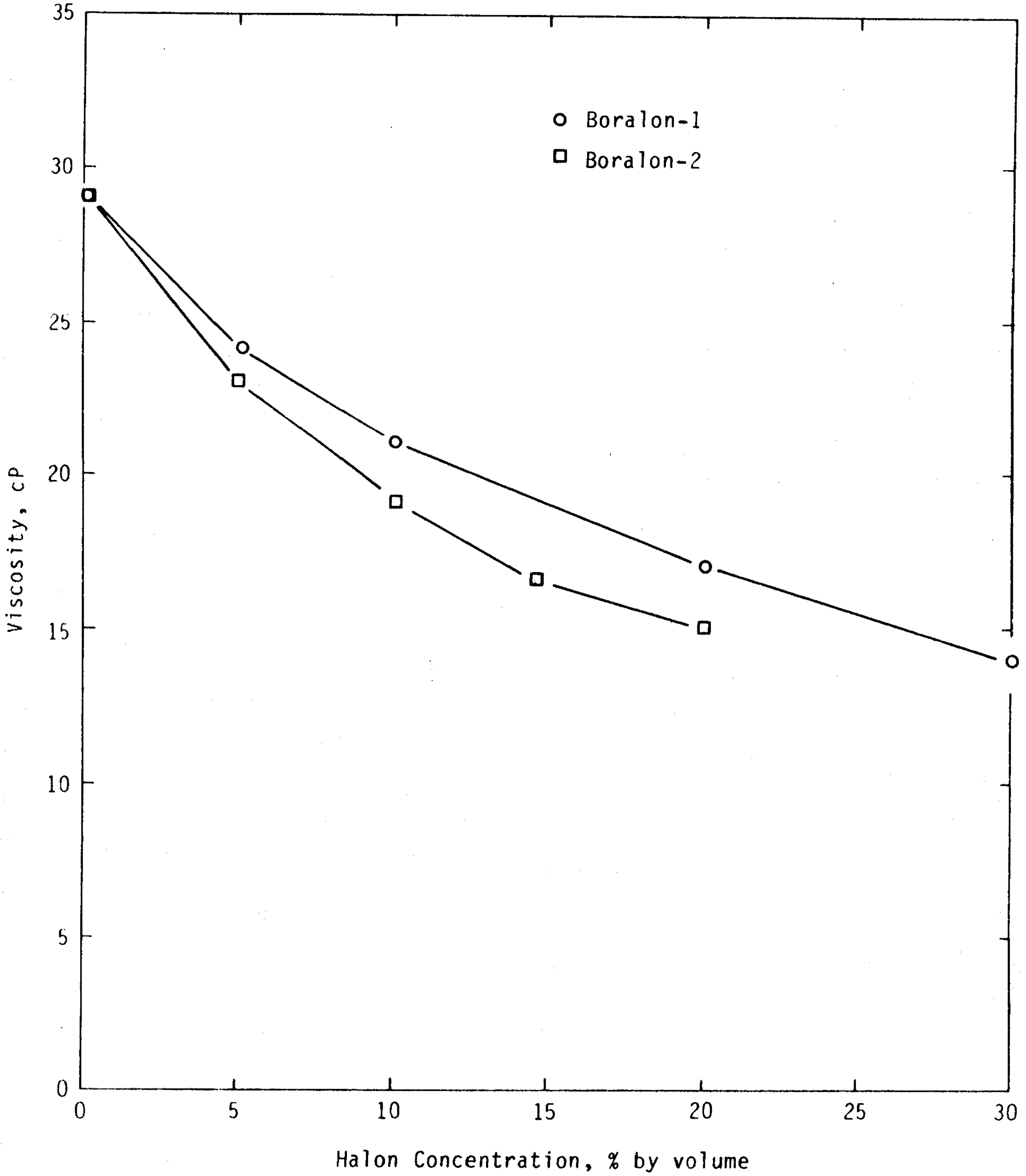


Figure 21. Viscosities of TMB/Halon Mixtures at 21°C as a Function of Percent by Volume Halon.

Loss of Volatiles

Weight losses of TMB/halon mixtures as a function of time were determined under conditions identical to those used for the viscosity studies. The results are presented in Table 17 and are graphed in Figure 22.

TABLE 17. WEIGHT LOSSES OF OPEN-AIR-AGED TMB/HALON MIXTURES.

Material	Weight loss, percent							
	1 day	2 day	3 day	6 day	7 day	8 day	9 day	10 day
TMB (control)	9.8	10.0	10.0	9.8	9.8	9.7	9.6	9.6
Boralon-2-5V	7.3	7.2	7.1	6.9	6.9	10.2	10.2	10.2
Boralon-2-10V	2.4	2.3	2.2	2.2	2.2	2.2	2.2	2.2
Boralon-2-15V	1.4	1.3	1.3	1.3	1.3	1.3	1.3	1.3
Boralon-2-20V	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1
Boralon-1-5V	10.9	15.1	15.0	14.9	14.9	14.9	14.8	14.8
Boralon-1-10V	9.6	17.2	16.9	21.3	21.3	21.3	21.2	21.2
Boralon-1-20V	21.4	21.3	21.0	28.2	28.1	28.1	28.0	28.0
Boralon-1-30V	33.8	37.8	37.8	37.5	37.5	37.4	37.3	37.3

In the absence of added halon, TMB lost weight rapidly and then reached a plateau. A similar rapid weight loss to approximately the same final value was seen in the Phase II study. As expected, the TMB/Halon 1211 mixtures lost weight rapidly as the highly volatile halon evaporated. The weight losses for the mixtures containing Halon 1211 were very near to those possible if only halon were lost. The mixtures containing Halon 2402, however, behaved anomalously. The weight losses for these latter materials was very small, much less than those observed for pure TMB. This behavior has been seen before (Reference 19).

Vapor Pressure

Experiments in both Phase II and Phase III show that the addition of Halon 2402 to TMB causes a significant decrease in the evaporation rate. This is unexpected since the vapor pressure of TMB is much less than that of

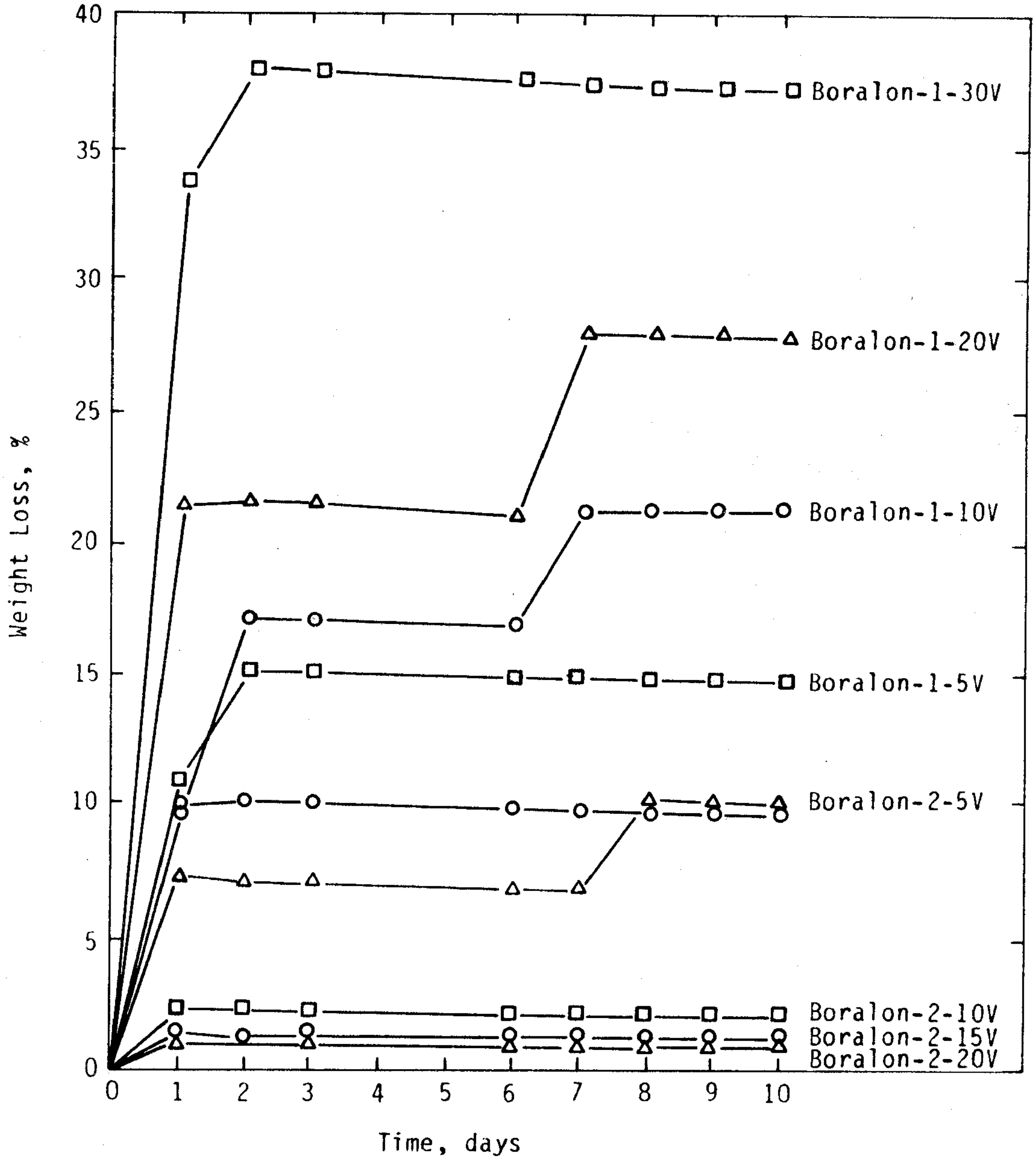


Figure 22. Weight Loss as a Function of Time for Open-Air Aging of TMB/Halon Mixtures.

Halon 2402, which should have been lost rapidly. To determine whether this phenomenon is caused by a decrease in vapor pressure of the mixture, vapor pressures of Boralon-2-10V and of TMB were determined as a function of temperature. The vapor pressures of TMB/Halon 1211 mixtures were too large to measure with the available equipment, and were much larger than those of pure TMB.

The vapor pressures were determined with an isoteniscope constructed specifically for mixtures (Figure 23). Most devices for vapor pressure measurement permit material to evaporate prior to the determination. With pure substances such a procedure is both acceptable and encouraged (to remove dissolved gases). With mixtures, however, loss of material can change the composition. The isoteniscope used permits the entire system, with the exception of a sample flask, to be evacuated before applying a vacuum to the sample itself. The sample fills the flask as nearly as possible so that there is little air space above it. Once the system is evacuated, the stopcock immediately above the flask is opened with the vacuum pump down again in a few seconds. The stopcock is closed and the sample allowed to sit under the "headspace" vacuum to degas. This procedure is repeated several times to remove dissolved gases. There is little loss of material in this operation. The vacuum pump is then isolated from the system and the equilibrium pressure is determined with a manometer.

The vapor pressures of pure TMB and of Boralon-2-10V at 25°C, 30°C, and 35°C are reported in Table 18. The functional dependence is shown in Figure 24.

TABLE 18. VAPOR PRESSURES OF TMB AND TMB/HALON 2402.

Agent	Vapor pressure, torr		
	25°C	30°C	35°C
TMB	28	44	51
Boralon-2-10V	80	87	112

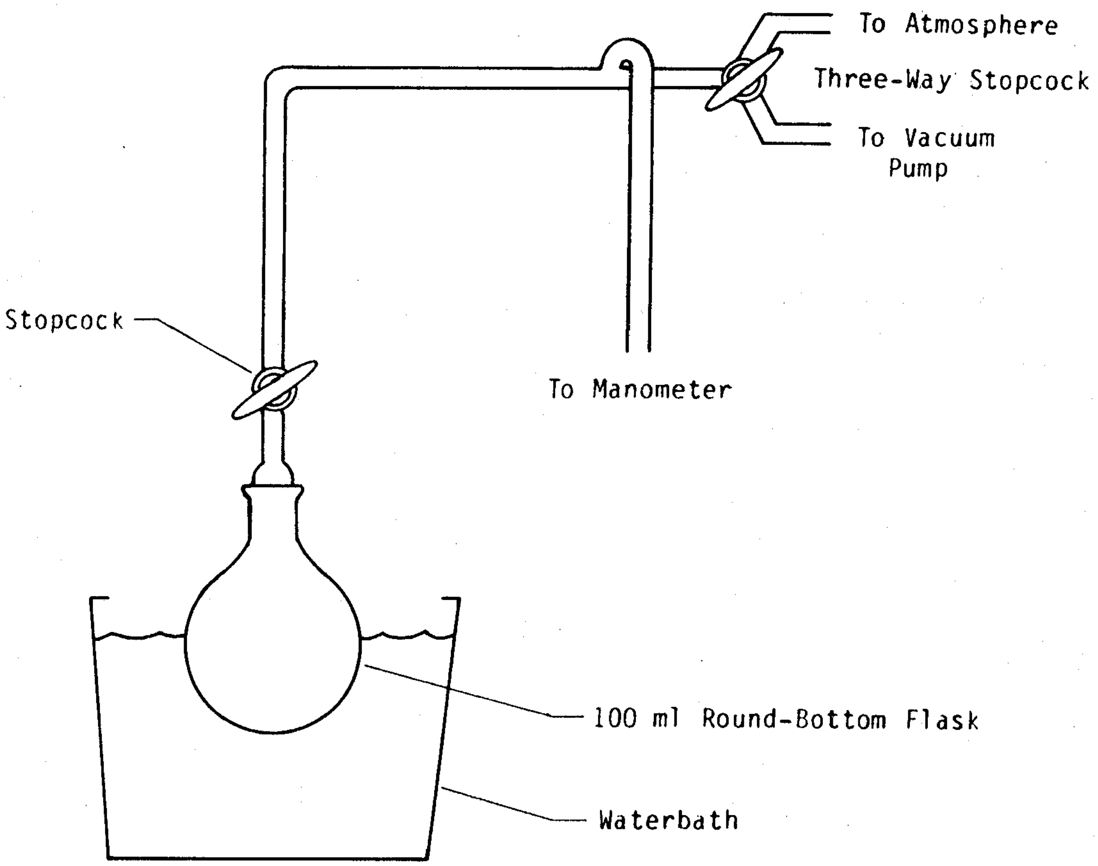


Figure 23. Isoteniscope Used for Vapor Pressure Measurements.

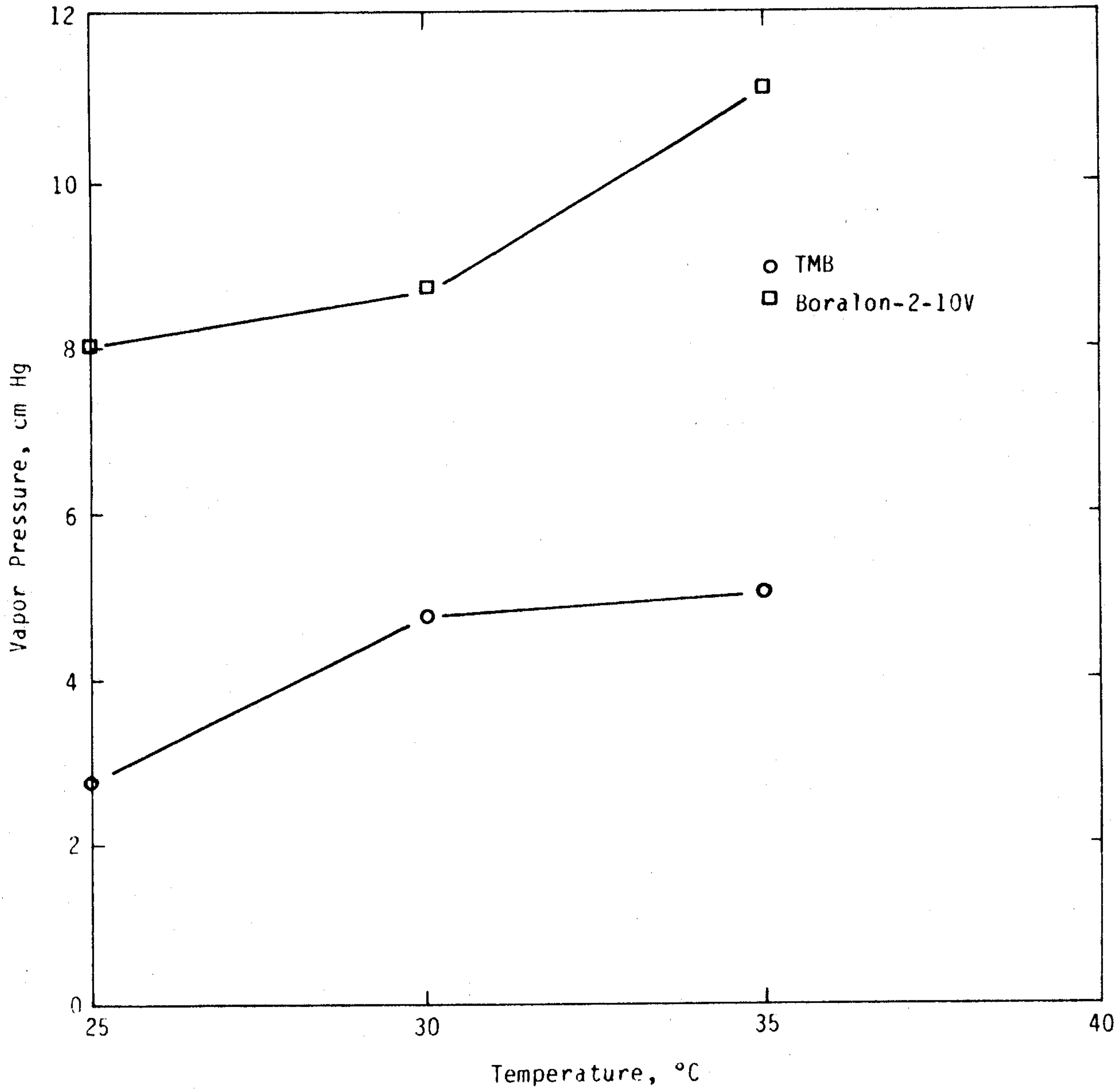


Figure 24. Vapor Pressure as a Function of Temperature for TMB and TMB/Halon 2402.

The vapor pressure of 28 torr at 25°C is in relatively good agreement with the value of 23.5 torr reported elsewhere (Reference 22). As mentioned earlier, the properties of technical grade TMB will vary from lot to lot.

The vapor pressure of TMB/Halon 2402 is significantly larger than that of TMB at all temperatures between 25°C and 35°C. These results appear to refute the explanation that the decreased evaporation rate of TMB/Halon 2402 mixtures is due to a lower vapor pressure. It could be, however, that on partial evaporation, the vapor pressures of mixtures containing Halon 2402 decrease to below that of pure TMB. To determine whether this is the case, Boralon-2-10V was permitted to evaporate under ambient conditions and the vapor pressure determined as a function of aging time. The vapor pressures of aged TMB were also determined as a control. The results are presented in Table 19 and are shown graphically in Figure 25.

Again, the vapor pressure of the TMB/Halon 2402 mixture is consistently higher than that of the pure TMB. At this point, there is no explanation for the lower evaporation rate observed for TMB, following addition of Halon 2402.

TABLE 19. VAPOR PRESSURES OF AGED TMB AND TMB/HALON 2402.

Agent	Vapor pressure, torr			
	0 h	24 h	48 h	168 h
TMB	36	30	27	21
Boralon-2-10V	96	51	54	55

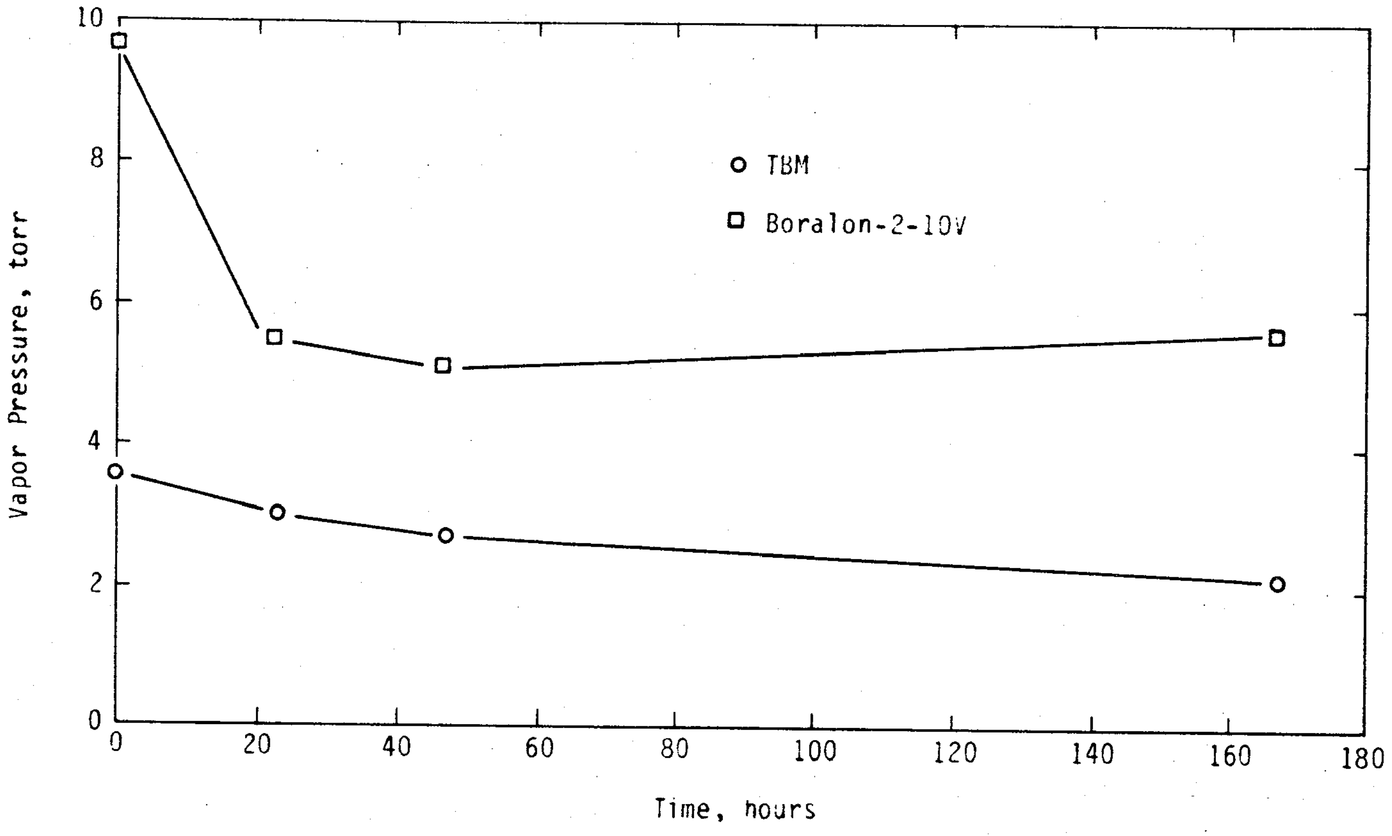


Figure 25. Vapor Pressure as a Function of Aging Time for TMB and TMB/Halon 2402.

Coating

As pointed out in an earlier report (Reference 19), the extinguishing feature apparently unique to TMB-containing Class D agents is the ability to form a tight, adherent coating over burning magnesium and other metals. It was proposed that this coating is due not only to formation of boron trioxide (B_2O_3) glass but also to the formation of compounds resulting from reduction of the boron (elemental boron, borides) and/or the formation of borates from the reaction of magnesium oxide and boron trioxide.

In an attempt to further characterize this coating, a series of X-Ray diffraction patterns of some possible coating materials (MgO, Mg_3N_2, MgB_2, MgB_6, B, H_3BO_3, B_2O_3) was obtained and compared with patterns obtained from magnesium extinguished with TMB and magnesium extinguished with water (possible when copious amounts are used). The powder patterns are shown in Figures 26 and 27. No diffraction patterns were determined for magnesium borates, which are difficult to prepare in their crystalline anhydrous forms. The only compounds which gave a good match were MgO, free magnesium, and MgB_6. The first two are not unexpected; however, presence of the latter boride proves that reduction is taking place during extinguishment. Elemental boron may have also been present; however, boron gives a poor X-Ray powder pattern and it is difficult to obtain a good comparison. The d-spacings from the powder diffraction patterns are given in Table 20. In some cases, more lines were observed than have been reported by others, this may be due to impurities.

Compatibility Tests

During Phase II, important studies on the compatibility of TMB and Halon 2402 with various elastomers and polymers were performed. To complete these studies, testing was conducted on one additional elastomer--Viton. Since Viton had been suggested as a possible gasket material for a TMB/halon extinguishing system, this testing was considered particularly important. The testing was performed identically to that described earlier (Reference 19) except that the Viton was permitted to sit in contact with the various chemicals for 69 days rather than for 67 days as done for the other elastomers. A

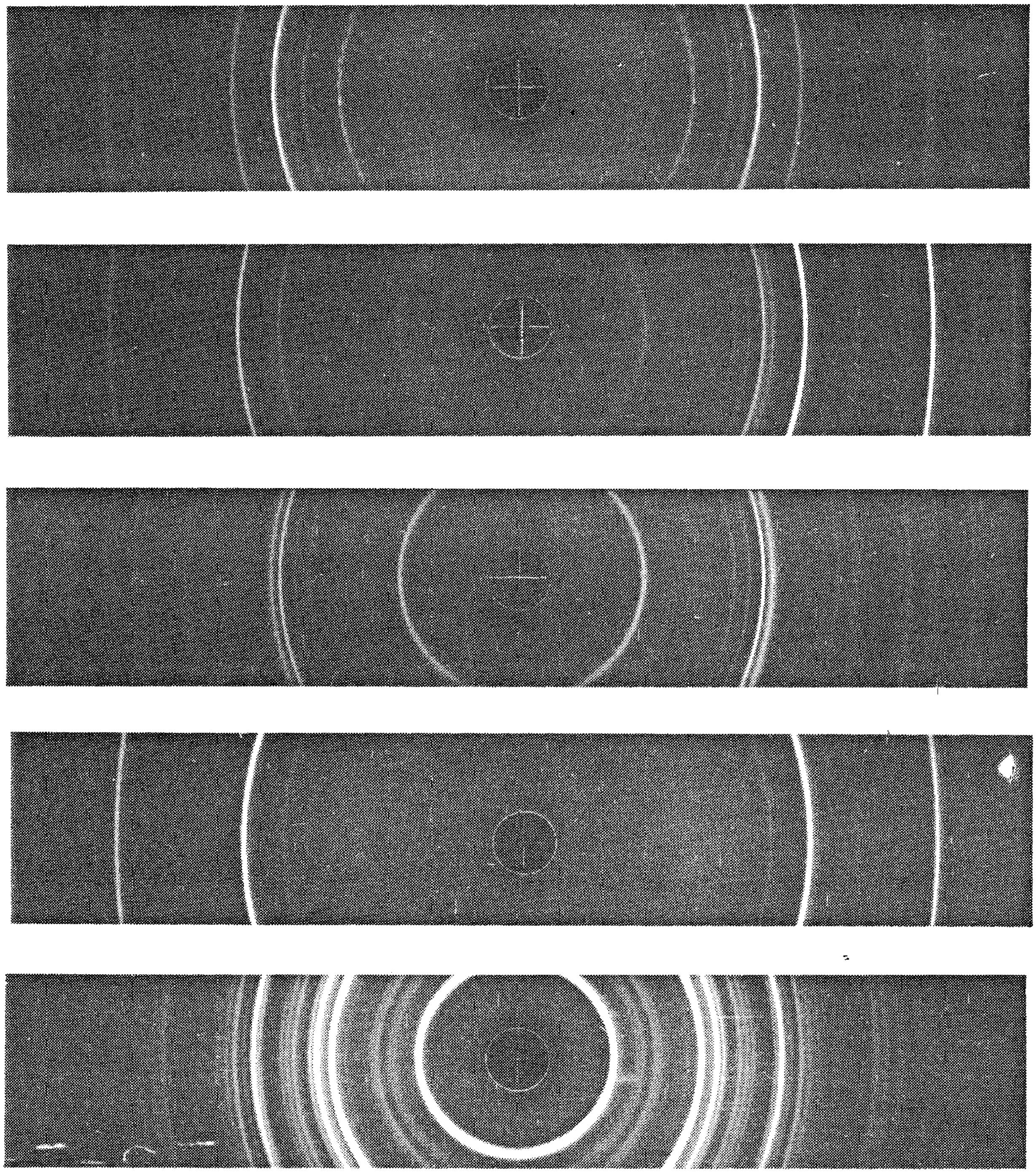


Figure 26. X-Ray Powder Patterns (From Top to Bottom: Magnesium Extinguished with TMB, Magnesium Extinguished with Water, Magnesium Metal, MgO, H_3BO_3).

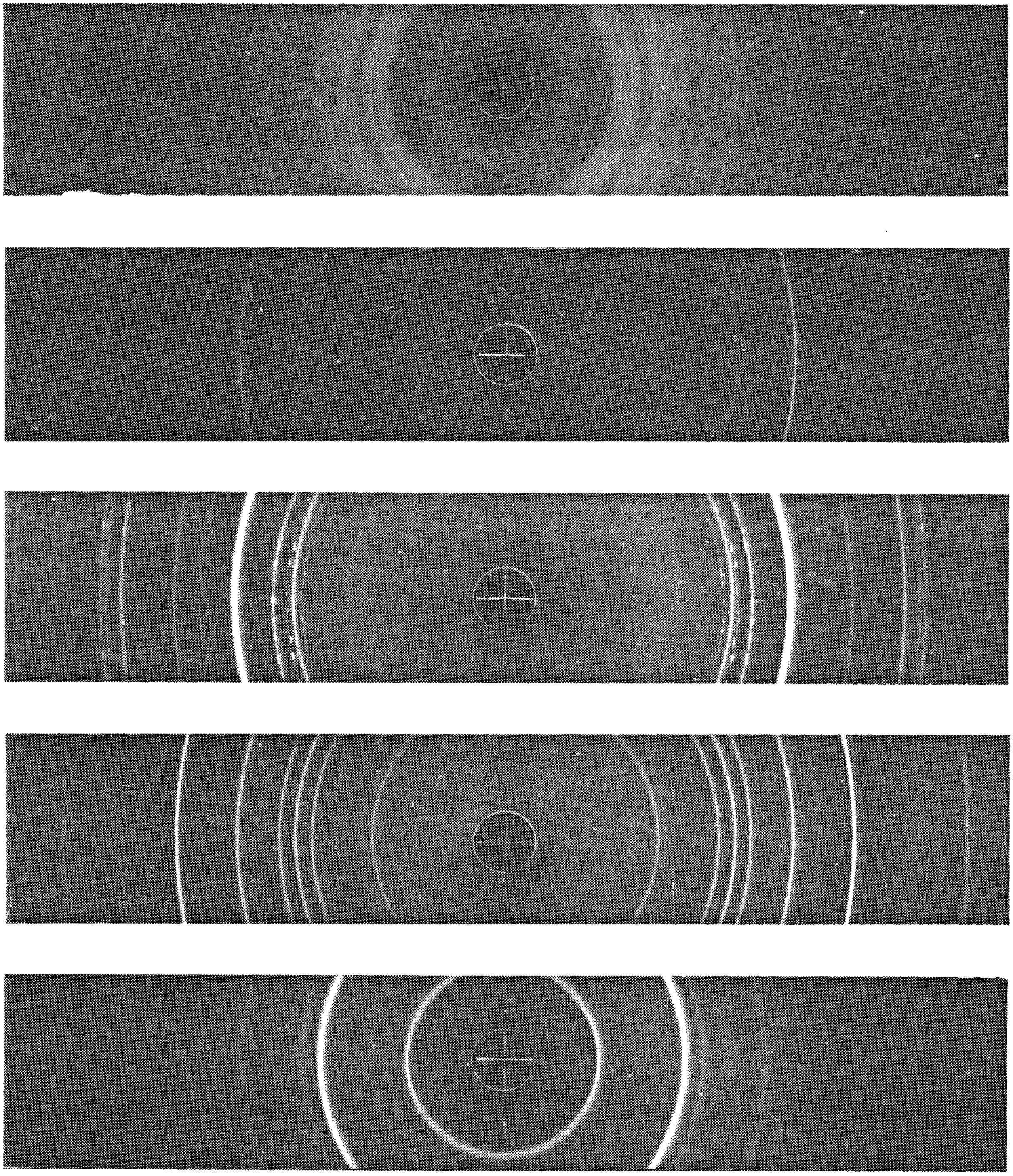


Figure 27. X-Ray Powder Patterns (From Top to Bottom: Elemental Boron, MgB_6, MgB_2, Mg_3N_2, B_2O_3).

TABLE 20. X-RAY POWDER PATTERN D-SPACINGS.

Material	D-Spacings
Mg/TMB	1.085, 1.185, 1.215, 1.340, 1.365, 1.470, 1.490, 1.551, 1.81, 1.90, 2.11, 2.45, 2.60, 2.77, 4.25, 4.70
Mg/H_2O	1.053, 1.218, 1.270, 1.489, 2.12, 2.37, 2.45, 2.61, 2.78, 4.70
MgO	1.054, 1.218, 1.270, 1.49, 2.11, 2.43
MgB_2	1.075, 1.161, 1.22, 1.25, 1.34, 1.37, 1.415, 1.475, 1.49, 1.543, 1.62, 1.763, 1.90, 2.13, 2.46, 2.62, 2.68, 2.79, 3.55, 3.82
B_2O_3	1.61, 1.69, 1.90, 1.97, 2.08, 2.24, 2.56, 2.91, 3.22, 3.47, 4.45, 5.01
Mg_3B_2	1.075, 1.115, 1.13, 1.225, 1.245, 1.267, 1.359, 1.439, 1.47, 1.50, 1.52, 1.619, 1.76, 1.82, 1.95, 2.13, 2.49, 2.67, 2.88, 3.85, 4.09, 5.00
H_3BO_3	1.175, 1.275, 1.335, 1.405, 1.485, 1.52, 1.57, 1.59, 1.65, 1.69, 1.89, 2.04, 2.10, 2.17, 2.25, 2.30, 2.50, 2.57, 2.66, 2.85, 2.95, 3.20, 3.45, 4.10, 4.25, 4.60, 4.80, 6.00
Mg	1.089, 1.183, 1.229, 1.31, 1.345, 1.368, 1.475, 1.499, 1.572, 1.61, 1.80, 1.90, 2.37, 2.46, 2.60, 2.78, 3.36, 4.80
B	1.36, 1.39, 1.435, 1.55, 1.68, 1.77, 1.94, 2.04, 2.34, 2.40, 2.50, 2.60, 2.74, 2.85, 3.19, 3.40, 3.55, 3.80, 4.20, 4.40, 4.70, 4.85, 5.05, 5.30, 5.45, 7.890, 8.80
MgB_6	1.14, 1.23, 1.44, 1.5, 1.54, 2.1, 2.45, 2.55, 2.85, 3.55, 4.2

Type A durometer was used. The results, presented in Table 21, show that of the elastomers tested, Viton ranks among the least compatible with TMB and Halon 2402. These results indicate that Viton cannot be used in extinguishing systems containing TMB/halon agents.

Agent Properties

As a preliminary investigation to the work necessary to produce a final military specification for agent procurement, some physical testing of TMB was performed. These tests may be used to determine lot-to-lot variations in TMB in the final procurement document. Note that a final military specification is not required in the present work.

TABLE 21. PROPERTY CHANGES FOR VITON IN CONTACT WITH AGENTS.[a]

Agent	Hardness Change	Change, percent			
		Weight	Length	Thickness	Width
TMB	-31.2(13)	113.4(28)	39.9(10)	55.0(18)	27.3(10)
Halon 2402	-14.0(9)	25.0(1)	4.0(16)	8.1(4)	6.9(45)
Boralon-2-10V	-36.4(11)	134.6(1)	42.9(9)	58.1(15)	29.8(13)

[a] Average deviations of last significant digit are given in parentheses.

NMR

Both proton and carbon-13 nuclear magnetic resonance (NMR) were determined on pure TMB from Aldrich Chemical Company. Both spectra were determined on a Varian FT-80 NMR with tetramethylsilane (TMS) as an internal reference. Deuterated benzene was used for the lock signal. Both spectra were very clean. The small 1:1:1 triplet downfield from the main peak in the C-13 spectrum is due to the C_6D_6 lock solvent. The proton spectrum (Figure 28) consists of a single peak (with spinning side bands) at 3.52 ppm downfield from TMS. The C-13 spectrum (Figure 29) also shows a single peak (again with spinning side bands) at 51.23 ppm downfield from TMS. These spectra indicate that NMR could be used to check sample purity. No spectral determination was performed on technical grade material.

Mass Spectrometry

The mass spectrum of TMB was determined in a solid sample probe on a Finegan Gas Chromatograph Mass Spectrometer (GCMS). The spectrum obtained is shown in Figure 30, along with some tentative assignments (Reference 23). The spectrum shows a number of interesting features. The presence of a possible CH_3OH^+ peak may indicate some hydrolysis to give methanol. The peaks due to trimethoxyboron ion, $(CH_3O)_3B^+$, and dimethoxyboron ion, $(CH_3O)_2B^+$, show that trimethoxyboron is given off during evaporation, a fact which provides one explanation for the viscosity increase during evaporation. The formation of trimethoxyboron is also believed to occur during extinguishment of magnesium

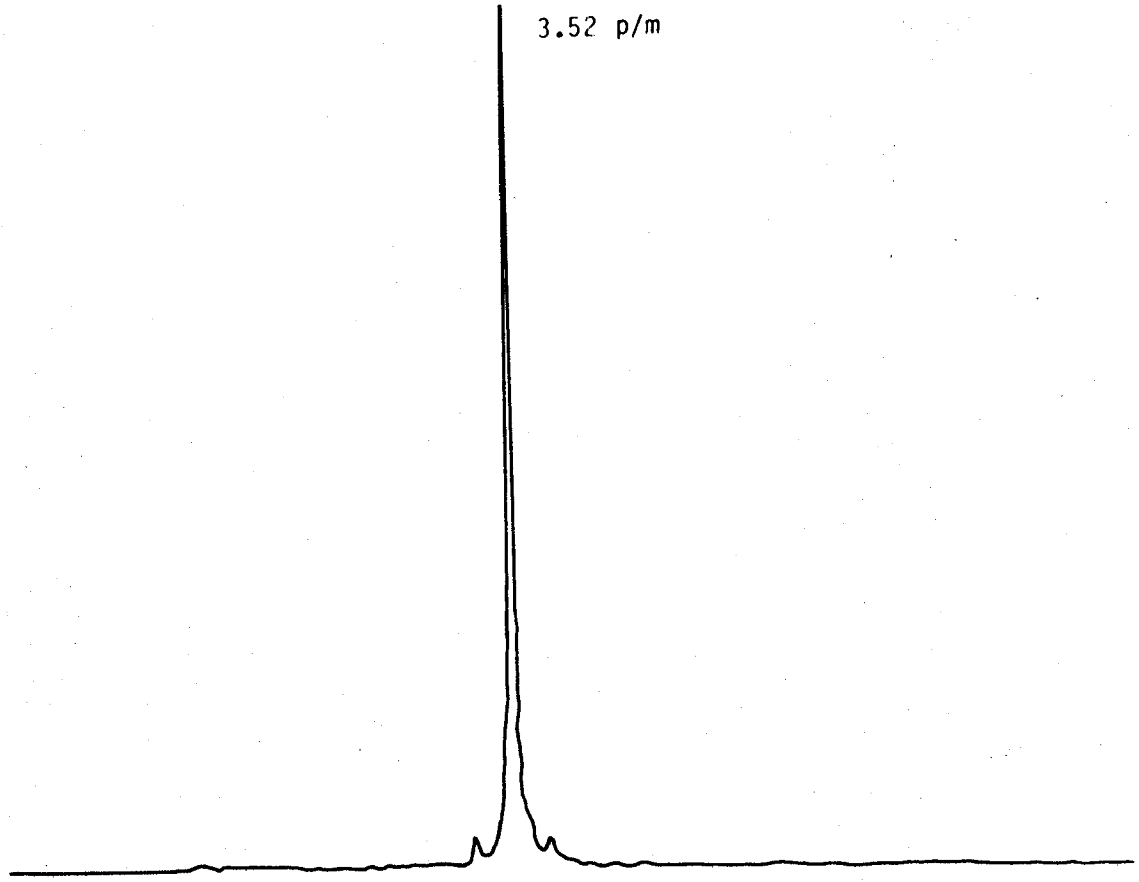


Figure 28. Proton NMR Spectrum of TMB.

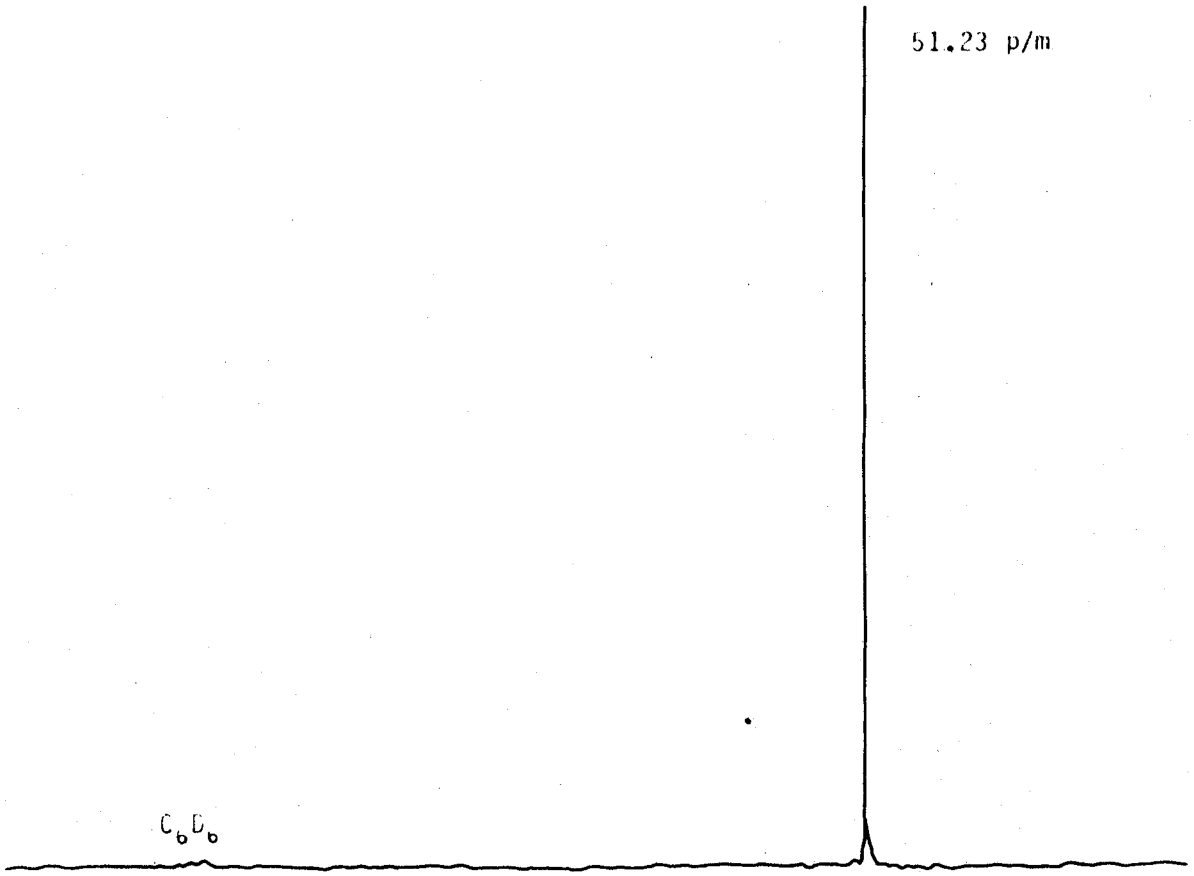


Figure 29. Carbon-13 NMR Spectrum of TMB.

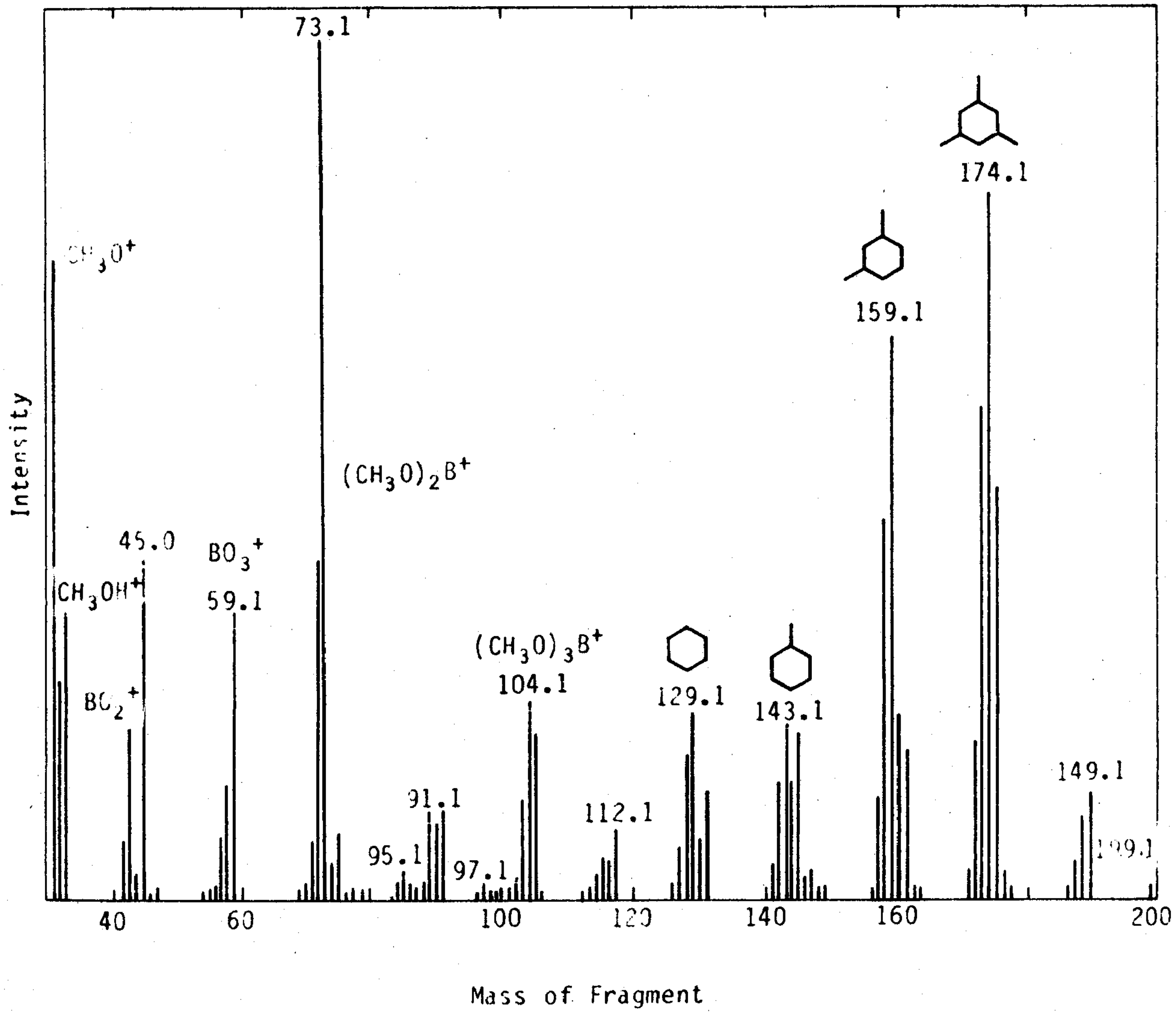


Figure 30. Mass Spectrum of TMB.

fires (Reference 24). Cyclic compounds are formed through the loss of methyl groups to produce $B_3O_3^+$ ion. One could imagine a similar process occurring during extinguishment to lay down a boron-rich oxide coating.

FIELD EXTINGUISHMENT TESTS

The test plans for the metal extinguishment tests were submitted as a deliverable on this project. A copy of those plans, which present descriptions and drawings of the apparatuses, is presented in Appendix D. Data sheets giving test parameters for each field test run during Phase III are presented in Appendix E. Only a brief summary of the test results are given here; however, extensive data are available in Appendix E, and this appendix should be consulted for further information. Only one large-scale, mixed-class B and D fire test was performed in Phase III. The remaining tests of this type will be performed in Phase IV as the required final testing.

Medium-Scale Agent Comparison Tests

The medium-scale agent comparison apparatus has been described in an earlier report (Reference 19). This apparatus was used to burn blocks of magnesium, occasionally mixed with titanium and aluminum. The mixed-metal tests showed that Boralon agents would not react violently with titanium as some had suspected.

The medium-scale test was then modified to add a liquid-fuel fire simultaneous to the metal fire. A 6.4-meter, 25.4-millimeter (21-foot, 1-inch) pipe, wrapped with SERA blanket for insulation, was led from a 208.20-liter (55-gallon) drum containing liquid fuel (JP-4 or JP-5) to the medium-scale fire pan. During Phase III, a 3785.4-liter (1000-gallon) tank was obtained for storage of JP-5 to obtain both JP-4 and JP-5 capabilities. Fuel was pumped to the pan during burns by a Tuthill NP700A Fill-Rite fuel pump. An RF&C F-90D, F/S 3028.32-liter (800-pound) check valve served as a flash arrester. The fuel was sometimes floated on water, but more often, was not. The maximum amount of liquid fuel used in any medium-scale tests was about 18.93-liters (5 gallons). The burning metal was occasionally separated from the burning liquid fuel, but was more often immersed in it. The medium-scale test gave strong evidence for the superiority of Boralon-1-30V, compared with any other agent tested. The testing showed unambiguously that application of AFFF foam to the burning liquid fuel, simultaneous with (or immediately preceding) application of Boralon-1-30V to the burning metal from two different extinguishing systems by two different fire fighters, could successfully extinguish mixed Class B and D fires. Note that this method does not use a dual-agent nozzle. Although immersion of magnesium in the fuel made the extinguishment more difficult, reliable extinguishment was still possible. The tests also indicated that better extinguishment could be obtained with Boralon-1-30V when it was applied in spurts, rather than continuously. Slightly better extinguishing ability was exhibited by the Boralon-1-30V when it was applied with a foam nozzle; however, to some extent, the Boralon agent is self-foaming. Boralon-1-30V covers and applies better than straight TMB.

Large-Scale Tests

The large-scale test system employing B-52 cowlings has been described earlier (Reference 19). The system was modified to burn a liquid fuel, simultaneously with the metal. A pan was installed underneath each cowling. During burns, the pans were filled using a 30.48-meter (100-foot) pipe and the same system described for the medium-scale apparatus. Most tests used only one cowling for the metal burn but both pans for the liquid fuel. A single large-scale Class B and D test was conducted during Phase III. This test showed that Boralon-1-30V was capable of extinguishing large-scale Class B and D fires when applied with AFFF, either sequentially or simultaneously. The remaining tests of this type will be conducted as the final testing required in Phase IV.

PHASE III CONCLUSIONS AND RECOMMENDATIONS

All testing indicates that TMB gives unsurpassed Class D fire suppression capabilities against fires of magnesium, in the presence or absence of titanium and/or aluminum. The negative characteristics of TMB can, to a large extent, be completely eliminated through the addition of halons and through the design of proper delivery systems. Halon addition can virtually eliminate TMB flammability and can lessen adverse aging properties. Proper engineering of a delivery system, which will be discussed in the Phase IV portion of the final report, can eliminate most of the remaining aging problems, as well as problems encountered with hydrolysis and material incompatibility.

Tests show that Halon 2402 can be added to the point that it constitutes 10 percent by volume of the final TMB/halon mixture before adverse effects are encountered. The concentration of Halon 1211 can be as large as 30 percent by volume. The latter mixture, Boralon-1-30V gives the best extinguishment and properties of any agent tested. The large halon concentration in Boralon-1-30V virtually eliminates any secondary fire and, as long as the agent is protected from evaporation, the material should remain nonflammable indefinitely. The volatile Halon 1211 causes this agent to partially foam to give an improved coverage and penetration and to enhance the spray characteristics. Boralon-1 agents contain a halon agent that is in general use today within the Air Force. This fact means that more is known about the probable safety and environmental properties of Boralon-1 agents than about Boralon-2 agents, which contain a halon not in general use today. All Boralon agents can be used with AFFF foam for Class B and D fires, though Boralon agents must be applied to the metal portion of the fire and AFFF, to the liquid-fuel portions. Boralons are most effective when applied to burning metals in spurts and/or with a foam nozzle.

The breakdown products of the Boralons are those of the separate components--TMB and halon. In a fire environment, TMB will give boron trioxide, water, and carbon-containing combustion products (primarily carbon dioxide and carbon monoxide with small amounts of aldehydes and ketones). Some methanol and trimethoxyboroxine may be produced by the heat alone. Halons can give a variety of products including hydrohalic acids (HF, HCl, HBr), free halogens, and halogenated hydrocarbons. There is no indication that Boralons will give breakdown products which differ from those of TMB and halons themselves. Thus environmental and toxicity problems will be no greater than problems with TMB and halons, both accepted firefighting agents.

The corrosivity of the Boralons toward plastics and elastomers has been well-documented here and in the Phase II report (Reference 19). In general, plastics and elastomers should be avoided in any delivery system. There is no corrosivity toward metals. Evidence to date indicates that the Boralons are indefinitely stable in sealed, dry containers. Some slow hydrolysis of the halon component may occur owing to traces of moisture. This has been observed with halon fire extinguishing agents in the absence of TMB. The extinguishing system designed for Boralons is described in Section V. This system isolates the Boralon agent from air and water and does not permit contact between the agent and plastics or elastomers prior to agent delivery.

In summary, Boralon-1-30V, a mixture of 70 percent TMB and 30 percent Halon 1211, by volume, is recommended as the agent of choice for combating Class D fires. At \$1.73/lb for Halon 1211 and \$4.50/lb for TMB, Boralon-1-30V would run \$3.41/lb, \$297/ft^3, or \$39.72 gal for the raw materials only. Other Boralon agents, however, give acceptable extinguishments and have acceptable properties.

SECTION V

PHASE IV--FINAL TESTING

TECHNICAL REQUIREMENTS FOR PHASE IV

Phases I and II, accomplished under Contract No. F29601-81-C-0013, identified several agents which extinguished metals fires; however, only one agent, TMB, could effectively extinguish such fires in both horizontal and vertical configurations. Other agents tested proved effective only on horizontal magnesium fires. TMB exhibits some adverse properties--primarily its flammability and poor aging characteristics. It was discovered in the Phase II effort that the addition of halons greatly decreases the flammability and improves certain other characteristics. In Phase III, Boralon-1-30V, a mixture containing 70 percent TMB and 30 percent Halon 1211 by volume, was shown to be superior to all other agents tested against fires containing JP-4, JP-5, aluminum, and/or titanium, in addition to magnesium. In Phase IV an agent delivery system will be designed and a prototype constructed; final full-scale testing of Boralon-1-30V will be performed. Hydrolysis and corrosion shall be considered. The final test shall include jet fuels and suspended, vertical configurations. Multiple agents shall be tested simultaneously to determine constructive or destructive interferences.

AGENT DELIVERY SYSTEM

The agent delivery system must be designed to overcome two problems which still exist with Boralon-1-30V. First, if allowed to sit in the open air, this agent will hydrolyze, lose volatiles, and become viscous. The presence of Halon 1211 decreases the tendency toward these adverse characteristics; nevertheless, Boralon-1-30V, like all other Boralon agents, will become too viscous to use if it is allowed to sit in the open. Second, Boralon-1-30V, like all other Boralon agents, attacks most plastics and elastomers. The agent must be kept out of contact with such materials. Any elastomers used should be of a chemical-resistant type. Hoses will not deteriorate rapidly and as long as they are washed out after use; there should be no problem.

To eliminate the hydrolysis and aging problem, a sealed system was chosen for the agent. This system contains a nickel diaphragm rated at 1034.25 kPa

(150 lb/in^2) that isolates the agent from ambient air. When a pressure of 1241.1 kPa (180 lb/in^2) is applied from an external nitrogen cylinder, the diaphragm ruptures, dispensing the Boralon-1-30V. The dimensions of the horizontal 113.56-liter (30-gallon) ASME code air tank used in this extinguishing system are 406.4 millimeters (16 inches) in diameter by 101.6 millimeters (40 inches) long by 549.3 millimeters (21 5/8 inches) high. The length includes the domed end caps. The shell length--the length disregarding the end caps--is 781.1 millimeters (30 3/4 inches). The height is the distance at the top of the tank from the ground and includes the 406.4-millimeter (16-inch) diameter as well as the legs. The tank is rated at 1379-kPa (200-lb/in^2) working pressure and weighs 58.97 kilograms (130 pounds). The system contains a 25.4-millimeter (1-inch) Schedule 80 dip tube, a 25.4-millimeter (1-inch) fill port, a nitrogen cylinder connected with the main tank by a steel braided line, a 1379-kPa (200-lb/in^2) fixed-pressure regulator, a 25.4-millimeter (1-inch) chemical firehose, a brass shutoff with nozzle, and a 25.4-millimeter (1-inch) union rupture disk at the top of the dip tube. Either a straight cone nozzle or a simple foam nozzle can be used with Boralon-1-30V. Nozzles containing small openings for the agent or complex mechanisms should not be used with any boralon agent. A drawing of the system is shown in Figure 31.

FINAL FIELD TESTS

The large-scale test apparatus used in the final field test is described under Phase II and Phase III (References 19 and 20). For the final tests, only Class B and D fire scenarios are used. Appendix F contains field test data sheets for the final tests; this material should be consulted for details.

Boralon-1-30V and AFFF foam, when applied separately but simultaneously (or nearly so), provide an outstanding combination of agents for the suppression of metal/liquid fuel fires. Sufficient AFFF must be used to knock down the liquid fuel fire to observe the burning magnesium (if necessary) before applying the Boralon-1-30V. The Boralon agent is best applied discontinuously in spurts. This procedure gives the best penetration and coverage. Though AFFF and Boralon are not incompatible, to the extent possible AFFF should not be applied to burning metal nor should TMB-containing agents be applied to burning liquid fuel. These techniques are described in Appendix G.

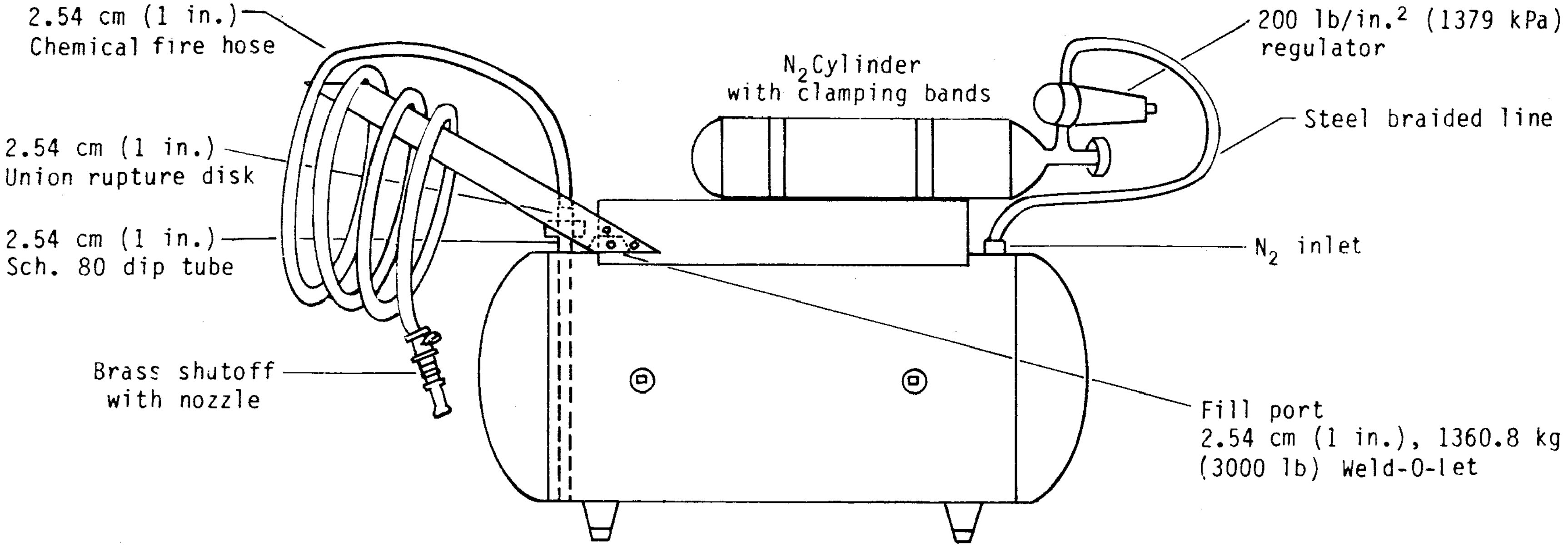


Figure 31. Agent Delivery System.

PHASE IV CONCLUSIONS AND RECOMMENDATIONS

The recommended agent for use with metal fires is Boralon-1-30V, consisting of 70 percent TMB and 30 percent Halon 1211 by volume. This agent should be delivered premixed in sealed extinguisher tanks containing a rupture diaphragm. The tanks should not be opened until needed for a fire, and they should not be recharged. Used tanks can be returned to the supplier in exchange for new sealed tanks.

To complete the work necessary to introduce this agent into the Department of Defense (DOD) system, several things must be done. As part of the present subtask, a draft specification for procurement is being written. During the coming year, this draft specification should be put in final form. System validation testing is necessary. Throw rates, throw patterns, nozzle designs, and ranges should be optimized. Reliability testing on the delivery system(s) is needed. This testing should include system aging, stress, and extremes in ambient conditions. The requirements for manufacturing the agent delivery systems and the agent mixture must be determined. A complete analysis of environmental concerns must be undertaken.

REFERENCES

1. ASTIA Document No. AD110685 and references therein.

2. Tuve, R. L., Gipef, R. L., Peterson, H. B., and Neill, R. R., **The Use of Trimethoxyboroxine for the Extinguishment of Metal Fires, Part I--Magnesium**, NRL Report 4933, Naval Research Laboratory, Washington, DC, July 1957.

3. Greenstein, L. M., and Richman, S. I., **A Study of Magnesium Fire Extinguishing Agents**, WADC Technical Report 55-170, Equipment Laboratory, Wright Air Development Center, Ohio, May 1955.

4. Whitacre, R. F., Jr., "A Feasibility Study of the Kinetics of Magnesium Combustion," M.S. Degree Thesis, June 1971, Purdue University.

5. Wilson, C., Plugge, M., and Zallen, D., **Extinguishing Agent for Metal Fire: Phase 1--Evaluation of Existing Agent**, Task Report for S.S. 3.03, Contract No. F29601-81-C-0013, Air Force Engineering and Services Center, Tyndall Air Force Base, Florida, September 1983.

6. Commerford, J. D., Chamberlain, D. L., Jr., and Shepherd, J. W., "Trimethoxyboroxine--An Extinguishing Agent for Metal Fires," **ACS Advances in Chemistry**, No. 23, American Chemical Society, Washington, DC, 1959, pp. 158-162.

7. Phillips, C. S. G., and Williams, R. J. P., **Inorganic Chemistry**, Vol. I, Oxford University Press, New York, 1965, p. 357.

8. **Halon 2402 Fluobrene**, Ausimont, Montedison S p A, Milano, Italy.

9. Lawrence, K. D., Gann, R. G., and Williams, F. W., **New Agents for Extinguishment of Magnesium Fires**, CEEDO-TR-78-19, Civil and Environmental Engineering Development Office, Tyndall Air Force Base, Florida, April 1978.

10. **JANAF Thermochemical Tables**, 2nd Ed., U.S. Government Printing Office, Washington, DC, 1971.

11. USSR Patent 831,727; **Chemical Abstracts**, No. 95: 171903n. "Amorphous Boron," Plyshevskii, Yu. S., Kerkher, T. E., Knysher, E. A., Lipinskii, I. E., and Vinogradov, A. A., May 23, 1981.

12. Markovsky, L. Y., Kondrashev, Y. D., and Kaputovskaya, G. V., "The Composition and the Chemical Properties of the Magnesium Borides," **Zhurnal Obschei Khimii, 25**, 1955, pp. 433-44.

13. Naslain, R., Guette, A., and Barrtet, M., "Magnesium diborides and tetraborides--crystallo-chemical considerations for the tetraborides," **Journal of Solid State Chemistry**, 8(1), 1973, pp. 68-85.

14. Hauck, D., and Meuller, F., "Thermochemistry of the Magnesium Oxide-Boron Oxide System," **Zeitschrift fuer Physikalische Chemie (Wiesbaden)**, 118(1), 1979, pp. 79-87.

15. Beltran, M. R., **Solid Fuel Ramjet, Fuels and Combustors**, Final Report, Contract F33615-83-C-2367, USAF Systems Command, Aero Propulsion Laboratory, Wright Patterson AFB, Ohio, 1984.

16. Williamson, H. V., and Conner, A. D., Cardox Corp., "Fire Extinguishing Apparatus with Delayed Action Control," U.S. Patent 2,758,657, August 14, 1956.

17. Schilling, C. L., Jr., Wesson, J. P., and Williams, T. C., "Polycarbosilane Precursors for Silicon Carbide," **Journal of Polymer Science: Polymer Symposium No. 70**, C. W. Allen, Editor, John Wiley & Sons, N.Y., 1983, pp. 121-128.

18. Sanders, H. J., "High-Tech Ceramics," **Chemical and Engineering News**, July 9, 1984, pp. 26-40.

19. Wilson, C., Tapscott, R. E., and Zallen, D. M., **Extinguishing Agent for Metal Fire: Phase II--Reformulation and Origination of Extinguishing Agents**, NMERI TA3-20, Task Report, Air Force Engineering and Services Center, Tyndall Air Force Base, Florida, September 1983.

20. "Standard Test Method for Flash and Fire Points by Cleveland Open Cup," ASTM D92-78, **1979 Annual Book of ASTM Standards**, Part 40, American Society for Testing and Materials, Philadelphia, 1979, pp. 15-17.

21. **BCF (Halon 1211), Systems Design Manual**, Imperial Chemical Industries Limited, Mond Division, Runcorn, Cheshire, England.

22. **Trimethoxyboroxine, Product Information**, Callery Chemical Company, Callery, Pennsylvania.

23. Lehman, W. J., Wilson, C. O. Jr., Shapiro, I., "The Mass Spectrum of Trimethylboroxine," **Journal of Inorganic and Nuclear Chemistry**, Volume 21, 1961, pp. 25-32.

24. Neill, Raymond R., "Trimethoxyboroxine for Magnesium Fires," **Quarterly of the National Fire Protection Association**, October 1960, pp. 178-181.

(The reverse of this page is blank.)

APPENDIX A
BIBLIOGRAPHY

Ballif, J. L., **Liquid Metals Fire Control Engineering Handbook**, Ford, Bacon, and Davis Utah, Inc., Salt Lake City, 1979.

Beidelman, J. A., **Liquid Nitrogen Fire Extinguishing System Test Report**, ANL-72-XX-9, May, 1972, Argonne National Laboratory, Argonne, Illinois.

Fire Protection for Combustible Metals, Data Sheet 1-567-79, National Safety Council, Revised 1979.

Fire Protection Handbook 15th Edition, National Fire Protection Agency, Quincy, Massachusetts, 1981.

Fisher, P. A., "Modern Manufacturing Uses of Magnesium Alloys," **Journal of Engineering Materials, Components, and Design**, Vol. 13, No. 3, March 1970, pp. 295-300.

Fox, D. G., **Investigation of Titanium Combustion Characteristics and Suppression Techniques**, AFAPL-TR-75-73, Air Force Aero Propulsion Laboratory, Wright-Patterson Air Force Base, Ohio, February 1976.

Friedman, R., and Levy, J. B., **Survey of Fundamental Knowledge of Mechanisms of Action of Flame-Extinguishing Agents**, WADC Technical Report No. 56-568, Wright Air Development Center (by Atlantic Research Corporation), Wright-Patterson Air Force Base, Ohio, January 1957.

Friedman, R., and Levy, J. B., "Mechanisms of Action of Chemical Agents for Flame Extinguishment," **Fire Research Abstracts and Reviews**, Vol. 1, 1959, pp. 81-88.

Fristrom, R. M., "Combustion Suppression," **Fire Research Abstracts and Reviews**, Vol. 9, 1967-1978, pp. 125-160.

Kurup, M. P. R., **A Fire Extinguishing Composition and a Method for Preparing the Same**, March 15, 1980, Indian Patent IN 147843.

Magnesium Data Sheet No. 426A, 1975, National Safety Council, Chicago.

McCormick J. W., and Schmitt, C. R., "Extinguishment of Selected Metal Fires Using Carbon Microspheroids," **Fire Technology**, Vol. 10, 1974, pp. 197-200.

Mellottee, H., Extinction of Metal Fires," **Revue Generale De Thermique**, Vol. 16, No. 186-187, June/July 1977, pp. 523-538.

Mensenauer, P., Ochs, G., Peppler, W., **Testing of Graphite-Based Extinguishing Powder for Use on Liquid Metal Fires**, (translated from German) DOE-tr-69, November 1977, USDOE Technical Information Center, Oak Ridge, Tennessee.

Nash, P., "A Dry Powder Extinguishing Agent for Magnesium Fires," **Institute of Fire Engineers Quarterly**, Vol. 23, No. 51, September 1963, pp. 275-276.

Storage, Handling, and Processing of Magnesium, NFPA 48, 1974.

Revillion, M., et al., "New Developments on the Extinction of Metal Fires in General and of Sodium Fires in Particular," **Proceedings**, 2nd International Symposium on Loss Prevention and Safety Promotion in the Process Industries, September 1977, pp. IX-481-IX486.

Riley, J. F., and Stauffer, E. E., **Extingusihing Agent for Combustible Metal Fires**,, U.S. Patent 3,985,658, October 1976.

Riley, J. F., and Stauffer, E. E., "Na-X, a New Fire Extinguishing Agent for Metal Fires," **Fire Technology**, Vol. 10, 1974, pp. 269-274.

Sarrut, J., **Improvements in or Relating to the Extinction of Metal Fires**, U.K. Patent 1,588,876, April 1951.

Schmitt, C. R., **Extinguishant for Metal Fires**, U.S. Patent 3,840,075, October 1974.

Schmitt, C. R., "Carbon Microspheroids as Extinguishing Agents for Metal Fires," **Journal of Fire and Flammability**, Vol. 5, June 1974, pp. 223-234.

Smith, A. J., and Lunney, A. J., **Comparison Tests for Extinguishing Media on Metal Fires**, AERE-P-6745, Atomic Energy Research Establishment, Harwell, England, April 1971.

Williams, F. A., "A Unified View of Fire Suppression," **Journal of Fire and Flammability**, Vol. 5, January 1974, pp. 54-63.

Zenatsky, E. D., "Extinguishing Agents for Combustible Metals and Special Chemicals," **Safety Maintenance**, Vol. 120, No. 2, August 1960, pp. 28-32.

APPENDIX B
ABSTRACTS OF LITERATURE

AD-B010 507

AIR FORCE AERO PROPULSION LAB WRIGHT-PATTERSON AFB OHIO

(U) Investigation of Titanium Combustion Characteristics and Suppression Techniques.

DESCRIPTIVE NOTE: Final rept. 1 Jan 74-1 Mar 75,

FEB 76 66P

PERSONAL AUTHORS: Fox,Duane G. ;

REPORT NO. AFAPL-TR-75-73

PROJECT NO. AF-3048

TASK NO. 304807

UNCLASSIFIED REPORT

ABSTRACT: (U) This test program studies the burning characteristics of titanium under air flow conditions. The flat plate titanium samples are ignited by molten titanium from an electrically heated ignitor. Air flow conditions that support sustained combustion of a single sample are determined. The burn rate is measured on all tests with steady state burning. Argon gas is shown to be a feasible extinguishing agent for a titanium fire. Quick injection of a sufficient amount of argon gas to maintain a 60% concentration by volume of argon results in quick suppression by oxygen depletion. Carbon dioxide (CO2), a common fire extinguishing agent, is shown to sustain titanium burning at an accelerated rate. The ultraviolet (UV) radiation emitted by burning titanium is shown to be of a sufficient intensity for existing UV fire detectors to detect at reasonable distances. (Author)

DESCRIPTORS: (U) (*Titanium, *Combustion), (*Argon, Fire extinguishing agents), (*Compressor blades, Combustion), Air flow, Burning rate, Flat plate models, Fire detectors, Ultraviolet detectors, Combustion chambers, Ultraviolet radiation, Emission spectra, Flames, Suppression, Test facilities, Instrumentation, Gas turbines

IAC NO. MCIC-113223'

IAC DOCUMENT TYPE: MCIC - HARD COPY --

IAC SUBJECT TERMS: M--(U)Unalloyed Titanium, Combustion, Ignition, Air, Flow Rate, Ultraviolet Radiation.;

AD- 609 341

BATTELLE MEMORIAL INST COLUMBUS OHIO DEFENSE METALS INFORMATION CENTER

(U) METHODS OF CONTROLLING AND EXTINGUISHING TITANIUM FIRES.

DESCRIPTIVE NOTE: Technical note,

JUL 64 5P

PERSONAL AUTHORS: Maykuth,D. J. ;

UNCLASSIFIED REPORT

SUPPLEMENTARY NOTE:

ABSTRACT: (U) The purpose of this note is simply to summarize the methods and materials which have been developed to date for the control and extinguishment of fires involving titanium metal. The problems of controling and extinguishing titanium fires are greatly compounded by the extremely high affinity of titanium for oxygen and nitrogen, and the fact that the oxides of titanium are readily soluble in the molten metal. Thus, heated titanium can readily reduce many of the compounds or liquids normally used as extinguishing agents, and the absence of a protective oxide film results in the presence of a continuously reactive surface on the molten metal.

DESCRIPTORS: (U) (*TITANIUM, FIRES), (*FIRES, TITANIUM), (*FIRE SAFETY, TITANIUM), FIRE EXTINGUISHERS, OXIDES, METALS, POWDER METALS, COMBUSTION, BURNING RATE, GRAPHITE, SAND, WATER, RARE GASES, STORAGE, FLAMMABILITY

IDENTIFIERS: (U) DOLOMITE, FIRE PREVENTION, FIRE HAZARDS

AD- 620 899

BUREAU OF MINES PITTSBURGH PA

(U) FIRE AND EXPLOSION HAZARDS OF FLIGHT VEHICLE COMBUSTIBLES.

DESCRIPTIVE NOTE: Quarterly progress rept. for 1 Jun-31 Aug 65,

AUG 65 7P

PERSONAL AUTHORS: Kuchta,J. M. ;Martindill,G. H. ;Spolan, I. ;

PROJECT NO. AF-8119

TASK NO. 811934

UNCLASSIFIED REPORT

SUPPLEMENTARY NOTE: See also AD-614 694.

ABSTRACT: (U) The study was initiated to determine the ignition and flammability characteristics of titanium and its alloys in air and with various halogenated hydrocarbon fire extinguishing agents. The following fire extinguishing materials are included: bromochloromethan - CH2BrCl, dibromodifluoromethane - CBr2F2, bromotrifluoromethane - CBrF3, 1,1,1,-trifluorobromochloroethane - CF3CHBrCl, 1,2,2-trifluoropentachloropropane - CCl3CF2CFCl2. Various halogenated hydrocarbon materials are known to be effective as fire extinguishing agents and are employed in current aircraft fire protection systems. The utilization of similar type agents is being considered for fire protection in advanced flight vehicles which make extensive use of titanium and its alloys. During the present report period, a literature search was conducted, necessary materials were acquired for the initial experimental work, and test apparatuses were assembled and calibrated. In addition, ignition temperature type experiments were initiated with the fire extinguishing materials (vapors) in contact with heated titanium metal in air, nitrogen, and argon atmospheres. For convenience, the present experimental work is divided into two phases: (1) Autoignition experiments in heated vessels. (2) Experiments with electrically heated wires. (Author)

DESCRIPTORS: (U) (*HALOGENATED HYDROCARBONS, FIRE EXTINGUISHERS), (*FIRE EXTINGUISHERS, AEROSPACE CRAFT), (*TITANIUM, FLAMMABILITY), AUTOIGNITION, TEST EQUIPMENT, EXPLOSIONS, HAZARDS, IGNITION, FIRE SAFELY

AD- 475 499

BUREAU OF MINES PITTSBURGH PA EXPLOSIVES RESEARCH CENTER

(U) FIRE AND EXPLOSION HAZARDS OF FLIGHT VEHICLE COMBUSTIBLES.

DESCRIPTIVE NOTE: Quarterly progress rept. no. 2, 1 Sep-30 Nov 65,

NOV 65 8P

PERSONAL AUTHORS: Kuchta ,J. M. ;Martindill ,G. H. ; Spolan,I. ;

CONTRACT NO. AF33(615)64-1007

PROJECT NO. AF-8119

TASK NO. 811934

UNCLASSIFIED REPORT

Distribution: No Foreign without approval of Aeronautical Systems Div., (AFSC), Wright-Patterson AFB, Ohio.

ABSTRACT: (U) This is the second quarterly report on an investigation of the ignition and flammability characteristics of titanium and its alloys with various halogenated hydrocarbons which are candidate fire extinguishing agents for some advanced flight vehicles. During the present report period, autoignition type experiments were conducted to determine the minimum temperatures at which samples of titanium sponge may react (glow) with the vapors of the extinguishing agents in quiescent air. The extinguishing fluids included bromochloromethane, dibromodifluoromethane, bromotrifluoromethane, 1,1,1-trifluorobromo- chloroethane, and 1,2,2,-trifluoro- opentachloropropane. In addition, wire ignition type experiments were performed to determine the reactivity of the decomposition vapors of two of the halogenated materials with electrically heated titanium wires. Various flow conditions were employed. The results presented indicate that reactivity, as evidenced by temperature rise, is greater with the decomposition vapors alone than with the vapors mixed with air. (Author)

DESCRIPTORS: (U) (*TITANIUM, *FLAMMABILITY), FIRES, TITANIUM ALLOYS, AUTOIGNITION, HALOGENATED HYDROCARBONS, VAPORS, HIGH TEMPERATURE, FIRE EXTINGUISHERS, BAROMETRIC PRESSURE, HAZARDS, CARBON DIOXIDE, FUELS, BROMINE COMPOUNDS, CHLORINE COMPOUNDS

AD- 479 178

BUREAU OF MINES PITTSBURGH PA EXPLOSIVES RESEARCH CENTER

(U) FIRE AND EXPLOSION HAZARDS OF FLIGHT VEHICLE COMBUSTIBLES.

DESCRIPTIVE NOTE: Quarterly progress rept. no. 3, 30 Nov 65-28 Feb 66,

FEB 66 5P

PERSONAL AUTHORS: Kuchta ,J. M. ;Martindill ,G. H. ; Spolan,I. ;

PROJECT NO. AF-8119

TASK NO. 811934

UNCLASSIFIED REPORT

Distribution: No Foreign without approval of Aeronautical Systems Div. (AFSC) Wright-Patterson AFB, Ohio 45433.

ABSTRACT: (U) This report is on an investigation of the ignition and flammability characteristics of titanium and its alloys with various halogenated hydrocarbons which are candidate fire extinguishing agents for some advanced flight vehicles. Wire ignition type experiments were conducted to determine reactivity of the decomposition vapors of three halogenated hydrocarbons with electrically heated titanium wires. RESULTS INDICATE VAPORS OF THE DECOMPOSED COMPOUNDS ARE MORE REACTIVE WITH TITANIUM THAN ARE THE UNDECOMPOSED VAPORS. Also, experiments were conducted to determine the compatibility of such halogenated hydrocarbons with heated titanium under simulated hydrocarbon fire conditions. The extinguishing fluids used in the wire ignition experiments were 1,1,1-trifluoro bromochloro ethane (CF3CHBrCl), 1,2,2-trifluoropentachloro propane (CCl3CF2CFCl2), and bromochloromethane (CH2BrCl). In the simulated hydrocarbon fire experiments, diboromodifluoromethane (CBr2F2) and bromotrifluoromethane (CBrF3) were used in addition to the above fluids. (Author)

DESCRIPTORS: (U) (*TITANIUM, *FLAMMABILITY), (*TITANIUM ALLOYS, FLAMMABILITY), EXPERIMENTAL DATA, LABORATORY EQUIPMENT, DECOMPOSITION, CHEMICAL REACTIONS, SIMULATION, HIGH TEMPERATURE, IGNITION, HALOGENATED HYDROCARBONS, VAPORS, EXPLOSIVES, FIRE EXTINGUISHERS, SAFETY, HAZARDS, ENVIRONMENTAL TESTS, JET ENGINE FUELS, AIRCRAFT FIRES, COMBUSTION

AD- 100 809

EARLE (FRANCIS) LABS INC PEEKSKILL N Y

(U) A STUDY OF MAGNESIUM FIRE EXTINGUISHING AGENTS

MAY 55 1V

PERSONAL AUTHORS: GREENSTEIN,L.M.;RICHMAN,S.I.;

CONTRACT NO. AF33 616 355

MONITOR: ASD
TR55 170

UNCLASSIFIED REPORT

DESCRIPTORS: (U) *FIRE EXTINGUISHERS, *MAGNESIUM, CHLORINE COMPOUNDS, FIRES, MATERIALS, METHANES (1 C), TESTS

IDENTIFIERS: (U) METHANES (1 C)

AD- 827 737

NAVAL AMMUNITION DEPOT CRANE IND

(U) DAMAGE CONTROL AND EXTINGUISHMENT TECHNIQUES FOR MAGNESIUM FLARE COMPOSITIONS,

67 13P

PERSONAL AUTHORS: Carper,W. E. ;

UNCLASSIFIED REPORT

Distribution: No Foreign without approval of Armed Services Explosives Safety Board, Washington, D. C. 20315.

SUPPLEMENTARY NOTE: Originally published in the Minutes of the Explosives Safety Seminar (9th), Naval Training Center, San Diego, Calif., 15-17 Aug 67. 1 Nov 67. (AD-824 044).

ABSTRACT: (U) Several incidents of accidental ignition of the Mk 24 Aircraft Parachute Flare have made it necessary to find a method to extinguish this flare. Earlier assumptions that this magnesium flare with its own oxidizer could not be extinguished had been discounted by the U. S. Air Force. The Air Force had been successful in extinguishing the flare with water. Tests were designed to determine the most effective approach to fighting a flare fire. These tests included various fire fighting agents, several methods of attacking the fire and variety of equipments capable of extinguishing the fire. The majority of the testing was concerned with single flares in open space as might be experienced on an airfield or a flight deck of an aircraft carrier. Limited testing was conducted on multiple flare fires in open space but no testing was done in confined areas such as magazines or ready service lockers. (Author)

DESCRIPTORS: (U) (*PARACHUTE FLARES, *SAFETY), AIRCRAFT FLARES, DAMAGE CONTROL, FIRE EXTINGUISHERS, FIRE SAFETY, MAGNESIUM, FIRES

IDENTIFIERS: (U) MARK-24 FLARES

AD- 138 832

NAVAL RESEARCH LAB WASHINGTON D C

(U) THE USE OF TRIMETHOXYBOROXINE FOR THE EXTINGUISHMENT OF METAL FIRES: PART I. MAGNESIUM

JUL 57 43P

PERSONAL AUTHORS: TUVE,R.L.;GIPE,R.L.;

REPORT NO. NRL-4933

UNCLASSIFIED REPORT

DESCRIPTORS: (U) (*BORON COMPOUNDS, MAGNESIUM ALLOYS), (*FIRE EXTINGUISHERS, BORON COMPOUNDS), PORTABLE EQUIPMENT, PHYSICAL PROPERTIES, MAGNESIUM, CHEMICAL REACTIONS, FIRES, AIRCRAFT

AD-A061 664

NAVAL RESEARCH LAB WASHINGTON D C

(U) New Agents for the Extinguishment of Magnesium Fires.

DESCRIPTIVE NOTE: Final rept. Aug 76-Sep 77,

APR 78 30P

PERSONAL AUTHORS: Lawrence,Kenneth D. ;Williams,Frederick W. ;Gann,Richard G. ;

REPORT NO. NRL-6180-376-KDL-FWW-NJS

CONTRACT NO. MIPR-FY8952-76-65017

PROJECT NO. 414N

TASK NO. 10

MONITOR: CEEDO
TR-78-19

UNCLASSIFIED REPORT

ABSTRACT: (U) Ground glass powders (frits) have been evaluated as possible suppressants for magnesium fires. Conceptually, these would melt and form a glass coating on the surface of the burning metal, isolating it from the oxygen supply. Some frits containing oxides of magnesium and lithium reacted violently with the burning magnesium. However, several low melting frits proved to be good suppressants and were better than commercial suppressants. (Author)

DESCRIPTORS: (U) *Fire extinguishing agents, *Aircraft fires, *Magnesium alloys, Aircraft tires, Wheels, Explosions, Landing, High velocity, Braking, Frit, Glass, Powders, Fire suppression, Lithium alloys, Melting

IDENTIFIERS: (U) LPN-AFCEC-PO-77-10, WUCEED0414N1005, PE64714F

AD-B048 234L

NAVAL WEAPONS CENTER CHINA LAKE CA

(U) Literature Review on Titanium Combustion and Extinction.

DESCRIPTIVE NOTE: Technical publication Jan-Sep 79,

JAN 80 53P

PERSONAL AUTHORS: Rhein,Robert A. ;Baldwin,James C. ;

REPORT NO. NWC-TP-6167

PROJECT NO. W0592001

TASK NO. W0592001

UNCLASSIFIED REPORT

Distribution limited to U.S. Gov't. agencies only; Test and Evaluation; 31 Jan 80. Other requests for this document must be referred to Commander, Naval Weapons Center, China Lake, CA 93555.

DESCRIPTORS: (U) *Ignition, *Titanium, *Literature surveys, *Powder metals, *Oxidation, Combustion, Extinction, Fire safety, Oxygen, Air, Fire extinguishing agents, Bulk materials, Jet engines, Compressors

IDENTIFIERS: (U) Titanium fires, Bulk titanium, PE63514N, LPN-A03P-03PA/008C/0W0592-001

AD- 058 606

SOUTHWEST RESEARCH INST SAN ANTONIO TEX

(U) INVESTIGATION OF MAGNESIUM FIRE-EXTINGUISHING AGENTS

JAN 54 1V

PERSONAL AUTHORS: MCCUTCHAN,ROY T.;

MONITOR: WADC
TR54 5

UNCLASSIFIED REPORT

USGO & CONT

DESCRIPTORS: (U) *AIRCRAFT FIRE CONTROL SYSTEMS, *FIRE EXTINGUISHERS, *MAGNESIUM, COMBUSTION, EFFECTIVENESS

AD- 857 695L 13/12 13/4

MISSOURI UNIV COLUMBIA ENGINEERING EXPERIMENT STATION

(U) Light-Weight Fire Extinguishing System Container.

DESCRIPTIVE NOTE: Final technical rept.,

DEC 55 147P

PERSONAL AUTHORS: Pauw, Adrian ;Sangster, William M. ; Crabtree, Robert G. ;

CONTRACT NO. AF 33(600)-26243

MONITOR: WADC
TR-55-338

UNCLASSIFIED REPORT

Distribution: Controlled: all requests to Commander, Aeronautical Systems Div., Attn: ASJT. Wright-Patterson AFB, Ohio 45433.

DESCRIPTORS: (U) (*FIRE EXTINGUISHERS, *CONTAINERS), PRESSURE, POLYESTER PLASTICS, WEIGHT, REDUCTION, CONFIGURATION, TENSILE PROPERTIES, METHANE, FLUORINE COMPOUNDS, VALVES, LEAKAGE(FLUID), CORROSION INHIBITION, COSTS, SAFETY VALVES, BROMINE COMPOUNDS, ALUMINUM ALLOYS, TITANIUM ALLOYS, MAGNESIUM ALLOYS, STEEL, GLASS TEXTILES, LAMINATED PLASTICS, TOUGHNESS, WELDABILITY, EPOXY RESINS

IDENTIFIERS: (U) METHANE/DIBROMODIFLUORO

AD- 414 945

MSA RESEARCH CORP CALLERY PA

(U) EXTINGUISHMENT OF ALKALI METAL FIRES.

DESCRIPTIVE NOTE: Quarterly progress rept. no. 5, 16 Mar-15 June 63,

AUG 63 3P

PERSONAL AUTHORS: Rodgers,S. J. ;

UNCLASSIFIED REPORT

SUPPLEMENTARY NOTE:

ABSTRACT: (U) An investigation was made of agents and techniques for extinguishment and control of fires resulting from leakage of high temperature and high pressure alkali metals under sea level and reduced atmospheric pressure environments. Characteristics of ignition and combustion at various absolute pressures and partial pressures of oxygen are an integral part of this investigation. Additional tests have been made with TEC powders. Results with this material are very encouraging. Work continued on the development of a suitable foam applicating system for alkali metal fires but a suitable system was not devised. (Author)

DESCRIPTORS: (U) (*ALKALI METALS, FIRES), (*FIRES, FIRE EXTINGUISHERS), IGNITION, COMBUSTION, PRESSURE, OXYGEN, FOAM, EXPANDED PLASTICS, ISOCYANATE PLASTICS, SODIUM, SODIUM ALLOYS, POTASSIUM ALLOYS, LITHIUM, SALTS

AD- 291 580

MSA RESEARCH CORP CALLERY PA

(U) EXTINGUISHMENT OF ALKALI METAL FIRES

JUN 62 1V

PERSONAL AUTHORS: RODGERS,S.J.;EVERSON,W.A.;

REPORT NO. 62 65

CONTRACT NO. AF33 657 8310

UNCLASSIFIED REPORT

ABSTRACT: (U) Contents: Review of current practices Progress on review of physical and chemical properties of alkali metals Effect of inert gas blanketing and low 02 partial pressures on alkali metal fires Extinguishment of alkali metal fires using in organic salt mixtures Extinguishment of alkali metal fires using inorganic salt foams Alkali metal jet stream ignition at various pressure conditions Bibliography

DESCRIPTORS: (U) *ALKALI METALS, *FIRE EXTINGUISHERS, BIBLIOGRAPHIES, CARBON DIOXIDE, CESIUM, COMBUSTION, CONTROL, FLAMES, FOAM, GASES, IGNITION, INORGANIC COMPOUNDS, JET STREAMS (METEOROLOGY), LITHIUM, OXYGEN, PHYSICAL PROPERTIES, POTASSIUM, PRESSURE, RUBIDIUM, SALTS, SODIUM, TEST EQUIPMENT, TEST METHODS

AD- 291 579

MSA RESEARCH CORP CALLERY PA

(U) EXTINGUISHMENT OF ALKALI METAL FIRES

OCT 62 1V

PERSONAL AUTHORS: RODGERS, S.J.;EVERSON, W.A.;

REPORT NO. 62 124

CONTRACT NO. AF33 657 8310

UNCLASSIFIED REPORT

ABSTRACT: (U) Contents: Effect of inert gas nket and ow 02 partial pressures on alkali metal fires Extinguishment of small scale fires Extinguishment of alkali metal fires using inorganic salt foam Alkali metal jet stream ignition at various pressure conditions

DESCRIPTORS: (U) *ALKALI METALS, *FIRE EXTINGUISHERS, CESIUM, COMBUSTION, CONTROL, CONTROLLED ATMOSPHERES, FLAMES, FOAM, GASES, IGNITION, INORGANIC COMPOUNDS, JET STREAMS (METEOROLOGY), LITHIUM, OXYGEN, POTASSIUM, PRESSURE, RUBIDIUM, SALTS, SODIUM, TEST EQUIPMENT, TEST METHODS, TESTS

AD- 291 579

AD- 284 026

ARMY ENGINEER RESEARCH AND DEVELOPMENT LABS FORT BELVOIR VA

(U) DEVELOPMENT AND ENGINEERING TEST REPORT, CHARGES, ANTIFREEZE, FIRE EXTINGUISHER, LITHIUM/CALCIUM CHLORIDE BASE

DESCRIPTIVE NOTE: Technical rept.

JUL 61 95P

PERSONAL AUTHORS: MALCOLM, JAMES E.;

REPORT NO. AERDL-1681

PROJECT NO. DA-8M76-04-109, DA-8-76-04-109

UNCLASSIFIED REPORT

ABSTRACT: (U) This report covers development and engineeringtest phases for water additive charges, antifreeze, fire extinguisher, lithium/calcium chloride base. The report summarizes literature surveys and laboratory tests made. It is concluded that: (a) A solution having 20.0% $CaCl_2$, 8.8% LiCl, and 71.2% H_2O composition on a weight basis and having a density of 1.2265 at 68 F is satisfactory as a candidate antifreeze salt for winterizing water to -65 F; (b) Sodium chromate at a concentration of 1,050 mg/l of solution effectively inhibits the corrosive effect of the above salt solution on Al, steel, brass, Zn, Mg, and Cu; (c) Lithium-chloride solutions (approximately 23% LiCl by weight in water) are effectively nonfreezing to below minus 65 F and except for higher cost are as applicable for application in antifreeze charges as the $CaCl_2$ LiCl mixture in solution with water; and (d) Dry packaging of salt charges including the inhibitor is feasible. (Author)

DESCRIPTORS: (U) *CALCIUM COMPOUNDS, *CHLORIDES, *FIRE EXTINGUISHERS, *FREEZING POINT DEPRESSANTS, *LITHIUM COMPOUNDS, ALUMINUM, BRASS, CHROMATES, COPPER, CORROSIVE LIQUIDS, MAGNESIUM, SODIUM COMPOUNDS, STEEL, ZINC

AD- 284 026

APPENDIX C

RESULTS OF MAGNESIUM EXTINGUISHMENT STRIP TESTS

Agent Tested	Time (sec)	Amount (grams)	Coating Appearance	Comments
Solids Which Extinguished				
MET-L-X	7	36	dark	time inexact
	24	75		some clogging
	40	165		some clogging
	50	91		
	72	148		uneven flow
	77	41		
Saran Resin F120	13	38	black fabric-like	
	13	72		blew it out?
	20	26		
	22	77		
	25	76		
lithium chloride	14	216	grey powdery	
	32	255		uneven flow
	82	134		difficult to apply
Foundry Flux 230	25	36	hard grey-black	
	26	94		
foundry flux	25	134	hard grey-black	
	66	38		nozzle clogged
sodium borate/PVC	28	180	grey	reignited
casein	36	144	thin black-brown	
TEC powder	37	81	grey/black/white	Mg fire red color
	38	55		
copper powder	41	133	black	
	56	211		long-lived glow
borax	42	84	white powder	
	78	63		ran out of agent
bentonite	42	66	thin grey-white	extinguished poorly
	45	65		

Agent Tested	Time (sec)	Amount (grams)	Coating Appearance	Comments
ammonium chloride with silica gel	50	132		completely burned?
dolomite	50	215	thin grey-white	
	70	163		
anhyd boric acid	51	67	hard glassy	
Monnex	53	86	heavy white	small amounts best
polyvinyl chloride	54	162	MgO appearance	burned completely?
ammonium phosphate	58	224	glassy,	
ammonium chloride	66	41	MgO-like	
	69	73		nozzle clogged
glass flake	60	85	thin glassy	sustained glow
	61	52		sparks, glow
iron powder	60	96	charcoal black	glow, sparking
calcium chloride	66	92	thick white	
	80	102		clogging
	102	16		clogged, total burn

Solids with Questionable Extinguishment

lithium fluoride	66	123	grey/brown/white	smothered?
	148	114		application uneven
LITH-X	137	205	MgO-like, black	burned completely?
	95	194		remained glowing
G-1 Powder	120	332	MgO-like	nozzle clogged
sand	64	576	MgO-like	
feldspar	113	216	thin grey	nozzle clogged
sodium borate	80	21	patchy, glassy	applies poorly
	139	89		poor application
anhydrous sodium carbonate	81	358	green hard	burned faster?

Agent Tested	Time (sec)	Amount (grams)	Coating Appearance	Comments
glass powder 200 mesh	105 79	78 33	shiny black	remained glowing completely burned?
lithium chloride with silica gel	56	96	hard grey	clogging
calcium chloride	90	149	hard grey-white	poor extinguishment
		Solids Which Did Not Extinguish		
Na-X		158	only MgO	
sodium chloride		287 201	only MgO	
glass beads		6	only MgO	
magnesium oxide		26	MgO	
perlite		31 61	only MgO	nozzle clogged
sucrose		306	only MgO	
vermiculite		70	only MgO	nozzle was removed
casein		148	thin brown-black	
Mg carbonate		78	grey powder	
Borester 20 with silica gel		115	MgO-like	
feldspar		415 183	agent and black	nozzle removed
casein/talc/ Mg carbonate		60	light coating	clogging
		Liquids		
TMB	10	94	shiny grey-black	blaster used
paraffin oil	30 35	27 18	black	large fire reignited with H_2O

Agent Tested	Time (sec)	Amount (grams)	Coating Appearance	Comments
*20 cSt silicone	25	34	light brown-white	long secondary fire
*5 cSt silicone	45	30	grey and black	long secondary fire
*silicone oil 510	30	31	black/white/brown	long secondary fire
*triethyl borate	30	40	hard black	secondary fire
*diisodecyl-phthalate	40	20	dark charcoal-like	long secondary fire
*ethylene glycol and boric acid	50	56	hard black	long secondary fire
CH_2BrCl & diisodecylphthalate	50	31	black	fire, sparking
	50	54		mist used
triethyl phosphite		10		no extinguishment
Flarex	38	358	thin black	
	60	455		long secondary fire
	112	204		time/amount inexact
	146	335		
	10	125		blaster used

Agents Which Could Not be Applied

Borester 20

75% TMB and 25% triethylphosphite

hydrated sodium carbonate

boron

Sandia foam

*Reignited during test.

APPENDIX D

TEST PLANS/PROCEDURES

SECTION I

TEST PLANS FOR MAGNESIUM FIRE TESTS--USE OF DIFFERENT EXTINGUISHING AGENTS

PURPOSE OF TESTS

To determine the following:

1. The flow rates of Metal X, TMB, TMB/10 percent 2402 at given pressures.

2. Minimum amounts of Metal X, TMB, TMB/10 percent 2402 needed to extinguish a magnesium fire.

3. Best (most effective) flow rates of Metal X, TMB, TMB/10 percent 2402 needed to extinguish a magnesium fire.

4. The effective extinguishing throw distance of Metal X, TMB, and TMB/10 percent 2402.

5. The best spray pattern for Metal X, TMB, TMB/10 percent 2402.

6. Can a cloud of 100 percent TMB effectively put out a magnesium fire?

METHOD OF TESTING

A 2- by 4-foot, welded steel pan (4 inches deep) will be used as a platform for the magnesium fires. This platform will be supported by four concrete cylindrical blocks (22 by 12 inches) and a series of concrete cinder blocks (15 1/2 by 7 1/2 inches) stacked on top of each other. This will raise the platform to 24 inches above the ground as shown in Figure D-1. Two torches will be mounted next to the platform and pointed toward the center of the pan (Figure D-2). The magnesium will be cut into lumps (approximately 1000 grams). Two to three lumps will be used per test. These will be positioned in an irregular pattern to simulate a concealed or confined fire. Different extinguishants and spray patterns will be tested, each test will be videotaped, and all visual observations recorded by test personnel.

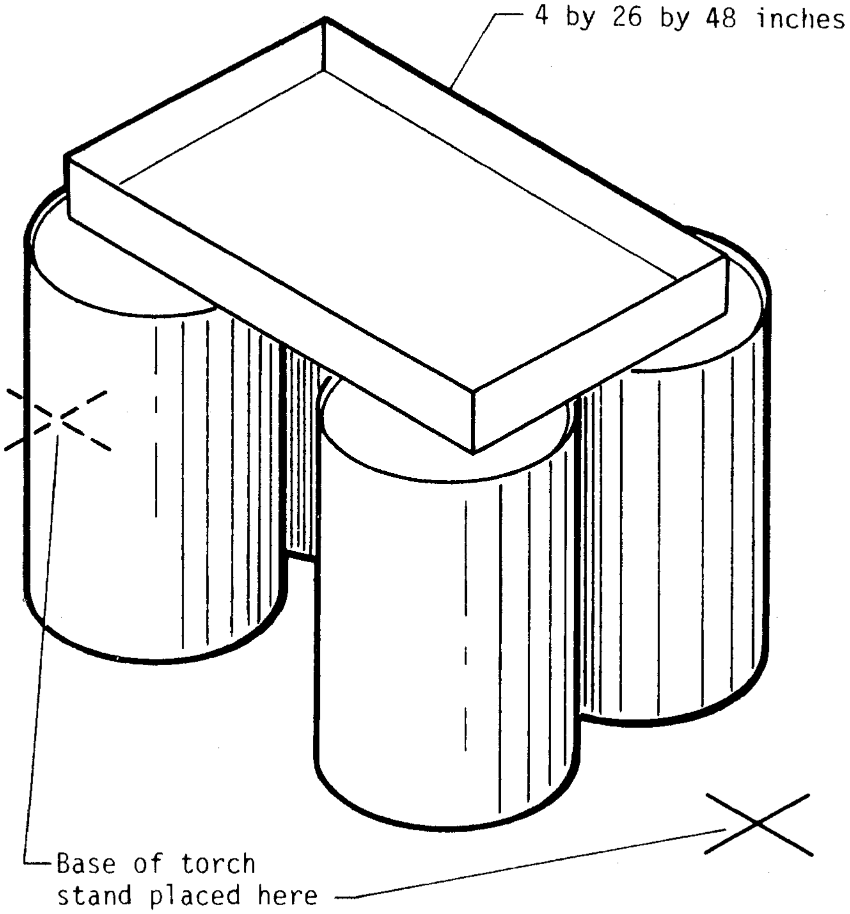


Figure D-1. Medium-Scale Magnesium Fire Test Apparatus.

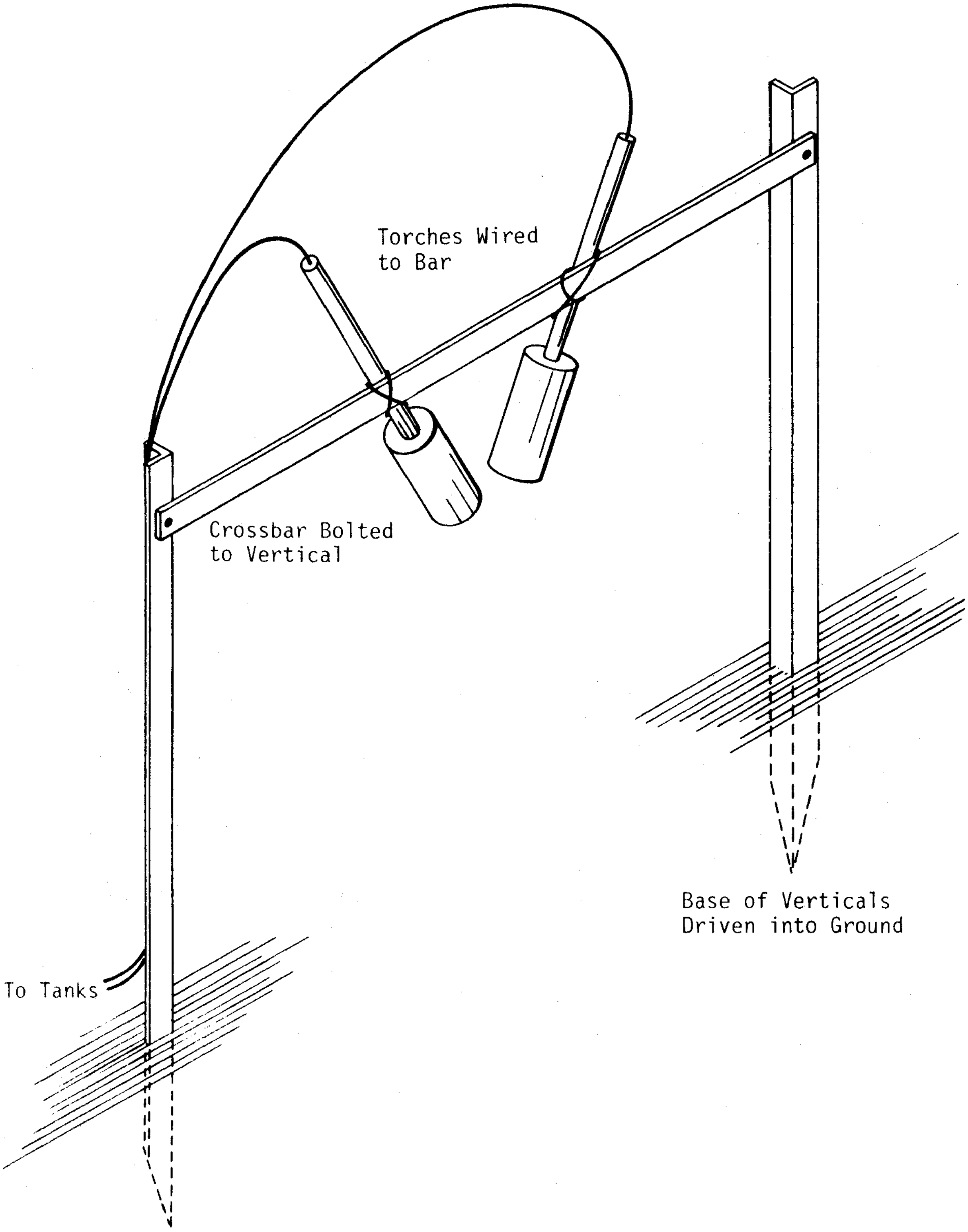


Figure D-2. Torch Configuration for Medium-Scale Test.

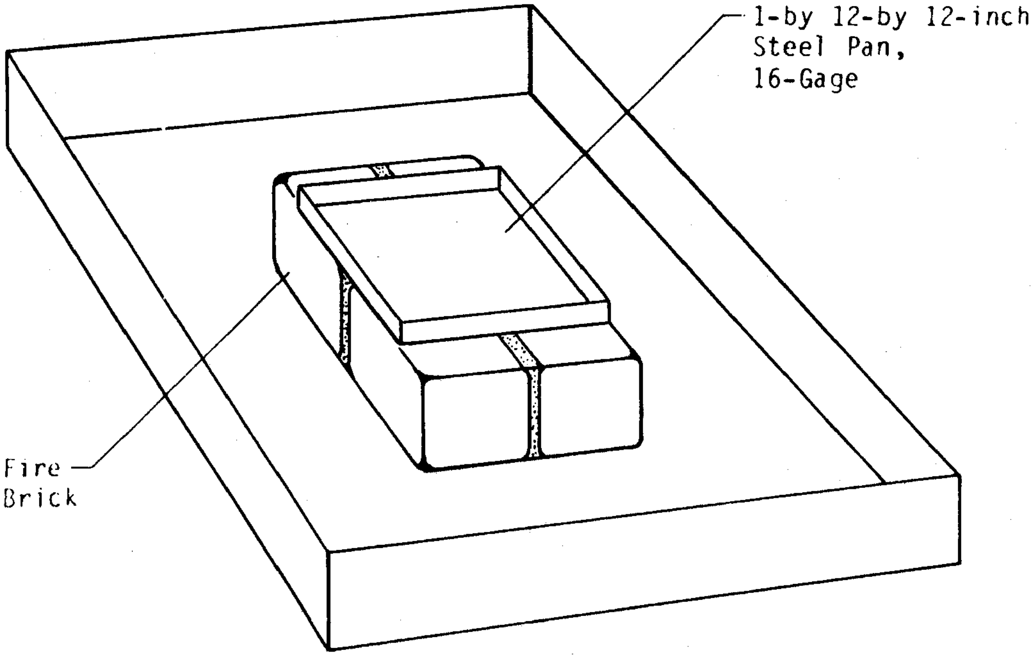


Figure D-3. Modification to Medium-Scale Test Apparatus.

METHODS OF MEASUREMENT

1. The flow rate of the extinguishing agents will be measured as follows:

A known amount of extinguishing agent will be loaded into the extinguishers (water-type first, then 10-gallon CB types), pressurized to a known pressure, and expelled into a container. This procedure will be timed with a stopwatch and the timing will continue until the extinguisher is empty. The mass flow rate will then be calculated by dividing the known time into the known mass quantity. This calibration will be performed for all types of extinguishing agents, nozzles, and test pressures.

2. The effective throw distance of each of the extinguishants will be determined by measuring the maximum distance from the fire that a solid straight stream can quench the fire. The distance will be measured on the ground before the test and markers will be placed at 5-foot intervals for a distance of 25 feet. Tests will be conducted by starting the spray from a maximum distance and then moving in toward the fire until the extinguishment has been completed.

3. The extinguishers will be weighed on a balance scale before and after each fire test to determine the amount of extinguishant used.

4. The weight of the magnesium samples will be determined before and after the fire test to determine the amount of magnesium the extinguishing agent saved.

ACCURACY OF RESULTS

Each fire test will be repeated at least three times, using the same procedure. Results of each test will be compared and averaged.

SUPERVISION

A test engineer will be present at each test and will supervise all tests.

PERSONNEL REQUIREMENTS

1. Test Conductor
    - a. Must wear fire protection suit.
    - b. Light torches and control flames.
    - c. Perform extinguishing test/operate extinguishers.
2. Test Engineer
    - a. Supervise test and record all data.
    - b. Operate camera, change titles, etc.
    - c. Enforce all safety rules and regulations.

APPENDIX D

SECTION II

LARGE SCALE MAGNESIUM FIRE TEST

PURPOSE OF TEST

To determine the following:

1. Severity of a large magnesium fire.

2. Feasibility of using a CB unit with 100 percent TMB and 90 percent TMB/10 percent 2402 at optimum pressures, using the nozzles best suited for the test.

3. Effectiveness of using Metal X and PKP on a large magnesium fire. These chemicals will unite on the P13 truck.

4. Establish firefighting methods when using 100 percent TMB, 90 percent TMB/10 percent 2402, and dry chemical powder on large magnesium fires. Chief A. Wozniak will be consulted on these methods.

METHOD OF TESTING

Two B-52 cowlings will be wired back to back and hung from an anchored pole stand. This stand will be adjustable and made so that the cowlings will be slightly above the firefighters' eye level. Refer to Figures D-4 and D-5 for stand details. The stand will be anchored to the ground by three legs which will be staked to the ground. A steel plate will be placed inside the cowlings to provide partial protection from the magnesium fire. The magnesium stack will consist of miscellaneous large pieces of magnesium, arranged on top of the steel plate. The weight of these magnesium samples will be recorded before the test. Torches will be mounted so that they can be readily removed. Two torches will be pointed into the stack from the front of the cowling. One torch will be mounted on top of the stack. No hand-held torches will be used. Each test will be videotaped and all visual observations recorded by test personnel.

METHOD OF MEASUREMENT

1. The magnesium samples will be weighted separately and the total weight recorded before each test. This procedure will be taken care of before the magnesium is brought to the fire site.

2. The amount of TMB or TMB/2402 used to extinguish the fire will be measured as follows: A CB unit (complete with wheeled cart) will be used as a test extinguisher. This unit will be weighed on a scale at the test site before and after each test and the weights recorded.

3. The amount of PKP or Metal X used to extinguish the fire will be measured by one of the following methods:

a. A flowmeter will be attached in-line to directly measure the mass flow rate.

b. Once the fire is extinguished, the tank will be depressurized and a rod will be placed in the dry powder to determine its depth change. The tank will then be repressurized.

c. Calibration tests will be run before the actual test and the flow rate determined. The time of extinguishment will then be recorded and used to determine the amount of dry chemical used.

ACCURACY OF TESTS

Because of the amount of magnesium and extinguishant used for each test, tests for each agent will be conducted only once.

SUPERVISION

A test engineer will be present at each test and will supervise all tests that are conducted.

PERSONNEL REQUIREMENTS

1. Test Conductors (2)

   a. Must wear fire protection suits.

b. Light torches and control flame.

c. Operate extinguishers. One firefighter will be operating the agent extinguisher and the other will back him up with a pressurized water line.

2. Test Engineer

a. Supervise test and record all data.

b. Run camera, change titles, etc.

c. Enforce all safety rules and regulations.

SAFETY REQUIREMENTS

1. Base Fire Department and Base Fire Chief will be called and informed of burn.

2. Area around burn will be cleared of all vegetation and combustibles for a distance of 25 feet.

3. A radio will be present at each test.

4. The P13 or XP13 units will be present at the test site and will be fully operational.

5. Nonfirefighters will stand 50 feet away from the fire and must wear magnesium safety glasses.

6. Firefighters will wear full silvers for the entire test.

7. One self-contained breathing apparatus will be present at the test site and will be fully operational.

8. A burn first-aid kit will be present at the test site and all test personnel will be briefed on its use.

9. A water source will be pressurized and operational to cool the molten metal after the test.

10. A drainage system of gravel and ditches will be constructed around the test site.

11. Wind direction will be noted and firefighters will <u>always</u> approach the fire from the upwind side.

12. Drinking water will be available at the test site.

13. All propane bottles will be protected behind a block wall from the fire. Propane lines will be covered when on the ground.

14. All personnel present at test site must be knowledgeable about magnesium hazards and first-aid practices.

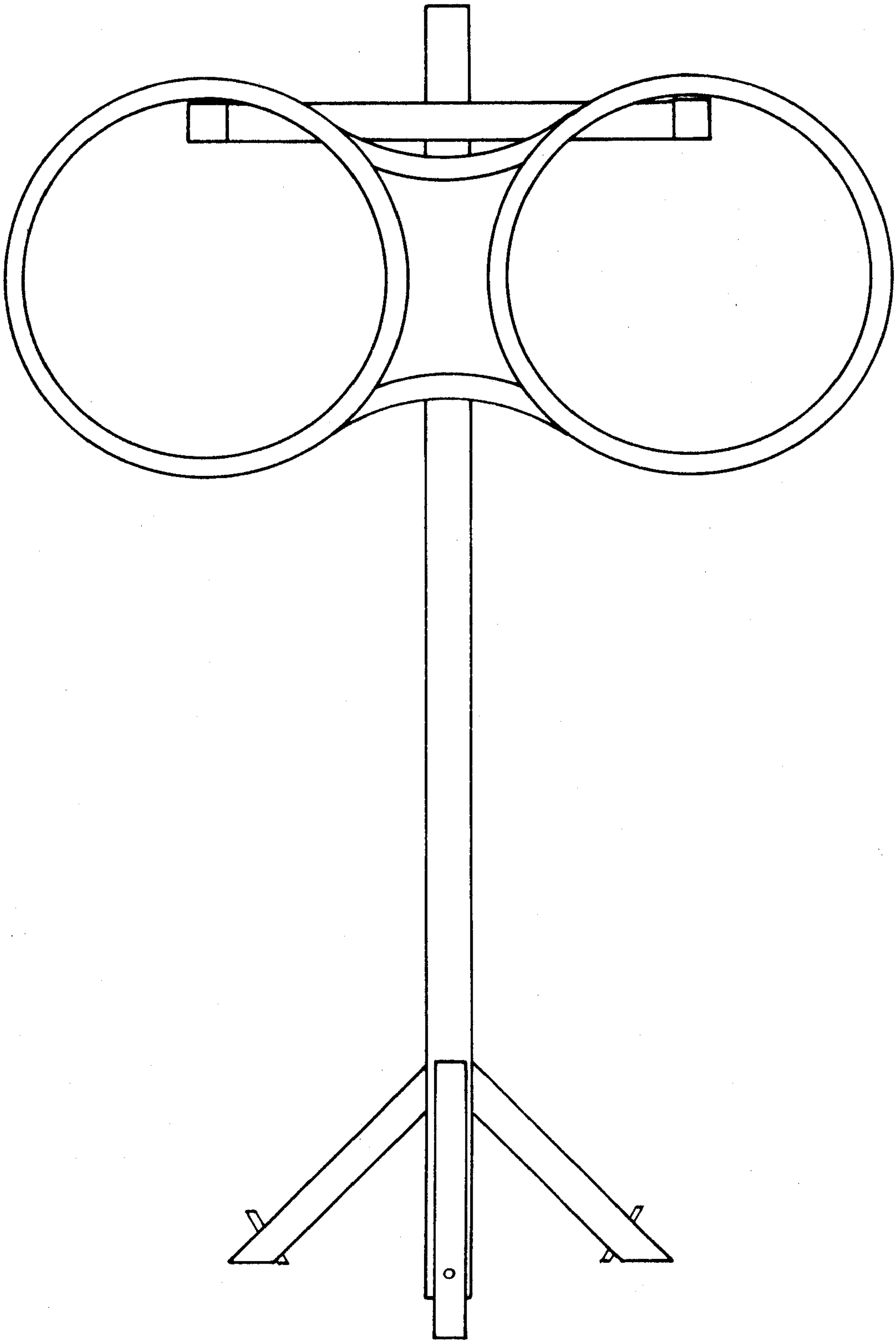


Figure D-4. Large-Scale Test Apparatus.

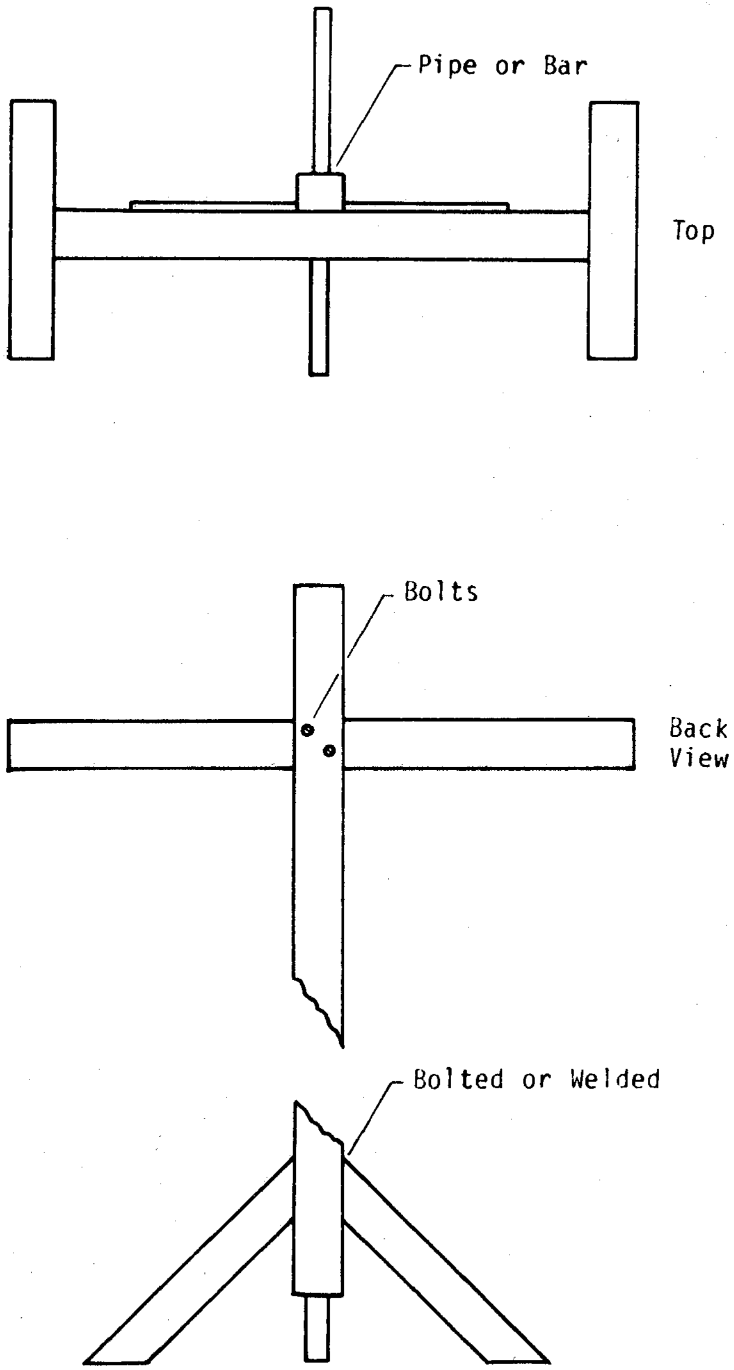


Figure D-5. Details of Large-Scale Test Apparatus.

APPENDIX D

SECTION III

LARGE-SCALE MAGNESIUM/JP4 FIRE--MODIFIED TEST PROCEDURE

MODIFICATIONS TO EXISTING TEST/TEST

Structure

1. To more fully simulate an actual aircraft crash fire, it was determined that JP4 or JP5 aviation fuel and the metals titanium and aluminum be added to this large-scale magnesium fire. This is done as follows:

   a. Scrap titanium and aluminum metals will be loaded into the existing B-52 cowlings, along with the magnesium. These metals will be burned together at one time.

   b. One to two steel fire pans (6 inches by 4 feet by 8 feet) will be placed under the cowling stand in such a way that the cowlings will be engulfed by the fuel fire.

2. The existing structure was modified so the cowlings could be hung lower to the ground. There is a clearance of 2 feet (adjustable to 3 feet) between the bottom of the cowlings and the steel fire pans.

3. A fuel line (65 feet long, 1 inch Schedule 40 steel pipe), equipped with a flash-arrester valve (rated at 3000 lb/in^2 at 850°F) installed near fuel-exit spout, will be used to transport the fuel from a 55-gallon drum. A 12 gal/min fuel pump will be used to transfer the fuel from the drum to the pan.

4. A movable torch stand (one level of standard scaffolding) will be placed in front of the cowling structure. Three to four torches will be mounted to this structure, each pointing into the cowling toward the stack of scrap metal.

5. The metal splash shield will be removed from under the cowling structure to make room for the fire pans.

Personnel Requirements

1. Two to three firefighters in full silvers will be required to perform this test. Each will be wearing a Comfo II respirator with the acid-gases cartridge installed.

2. A test engineer must be present at all times during the test. This engineer must be attired with safety shoes, hard hat, and magnesium goggles, and must have a Comfo II respirator (with acid-gases cartridges) ready at hand.

Test Procedure

1. Propane torches will be lit by personnel in full silvers. One person may be required to have a hand-held torch to light hard-to-reach areas of the metal scrap pile. This person will be in full silvers and wearing a Comfo II respirator (acid-gases cartridge).

2. When full metal ignition has been reached, the torches will be turned off and the torches and torch stand will be removed and placed off to the side out of the way.

3. The metal will be allowed to burn for approximately 1 minute.

4. The metal fire pan(s) (prefilled with approximately 80 gallons of H_2O) will then be filled with approximately 20 gallons of JP4 or JP5 aviation fuel. The fuel line will be removed and placed to one side.

5. The fuel will be ignited (if not already so).

6. The fuel will be allowed to burn for 20-30 seconds.

7. Two firefighters in full silvers will approach the fire. A layer of foam will be applied by one firefighter to knock down the fuel fire. The other firefighter will then direct his extinguishing agent (70 percent TMB/30 percent Halon 1211) toward the metal fire. Then both firefighters will fight both fires simultaneously.

8. Halon 1211 and Halon 2402 backup units will be available for use if the fire becomes uncontrollable.

9. The residue will be cooled with water.

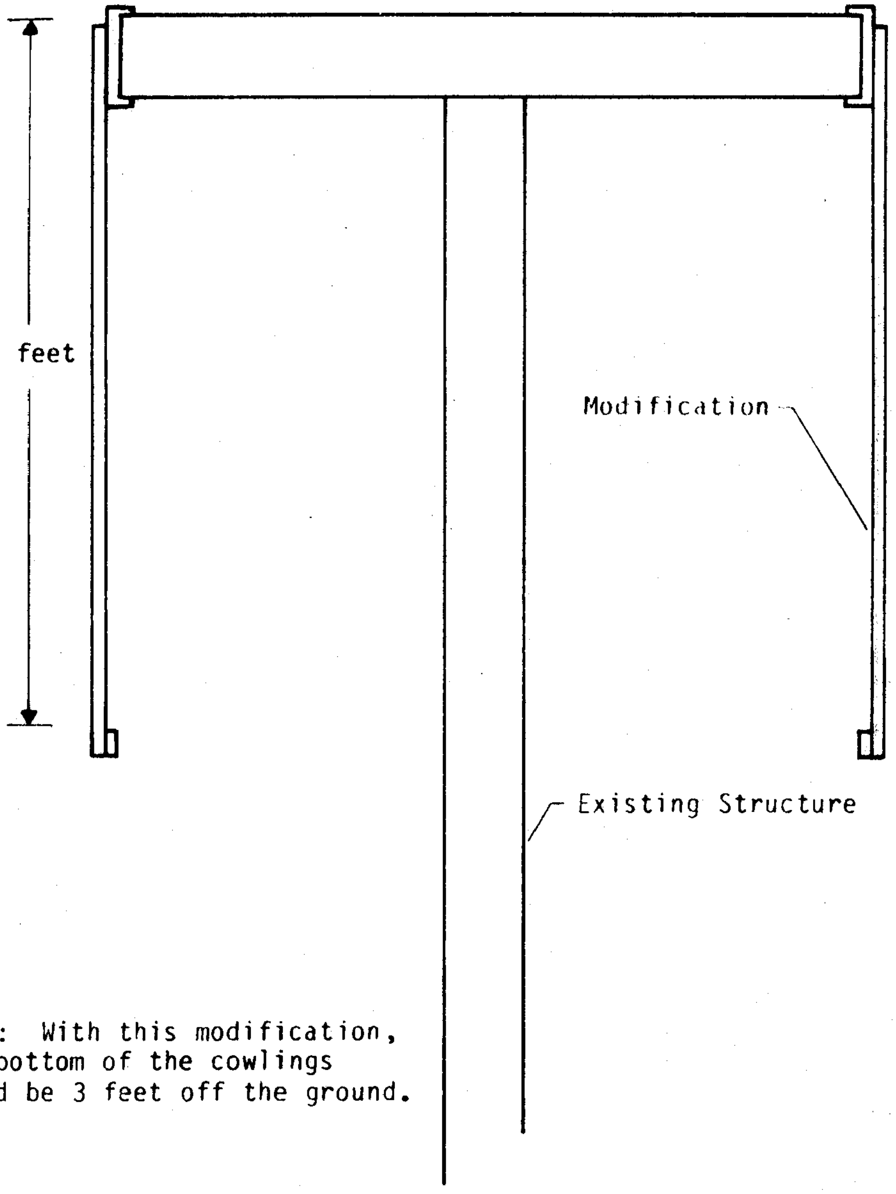


Figure D-6. Large-Scale Test Apparatus Modification.

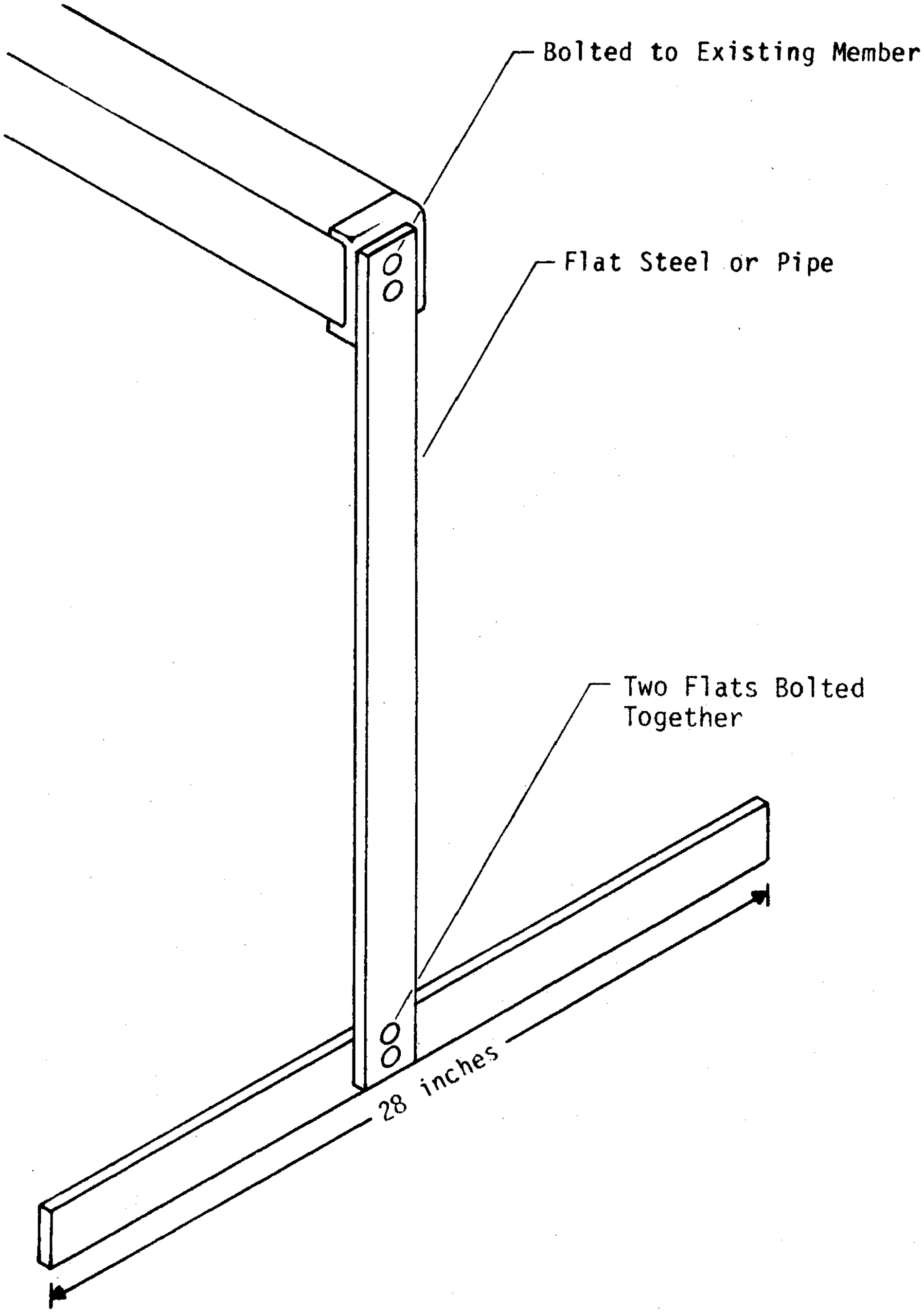


Figure D-7. Large-Scale Apparatus Option 1.

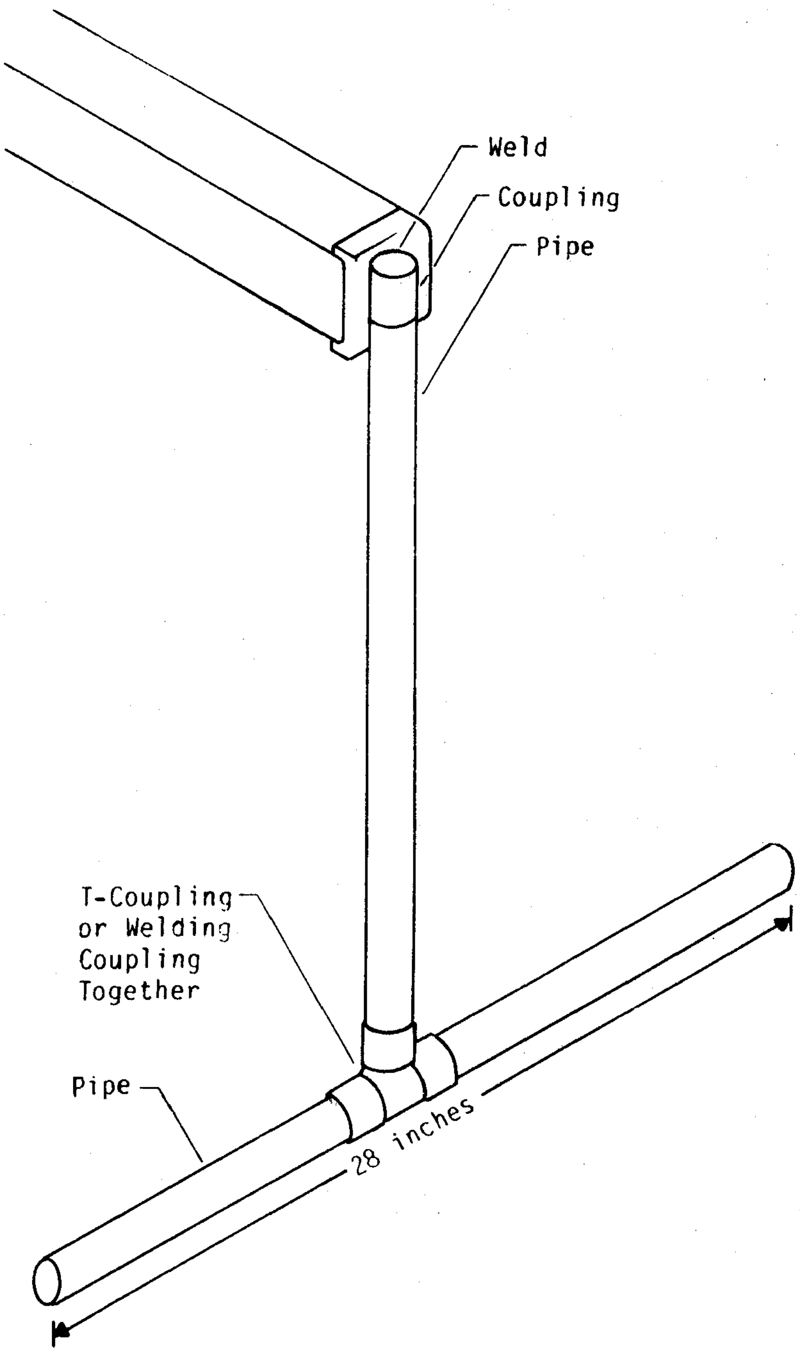


Figure D-8. Large-Scale Apparatus Option 2.

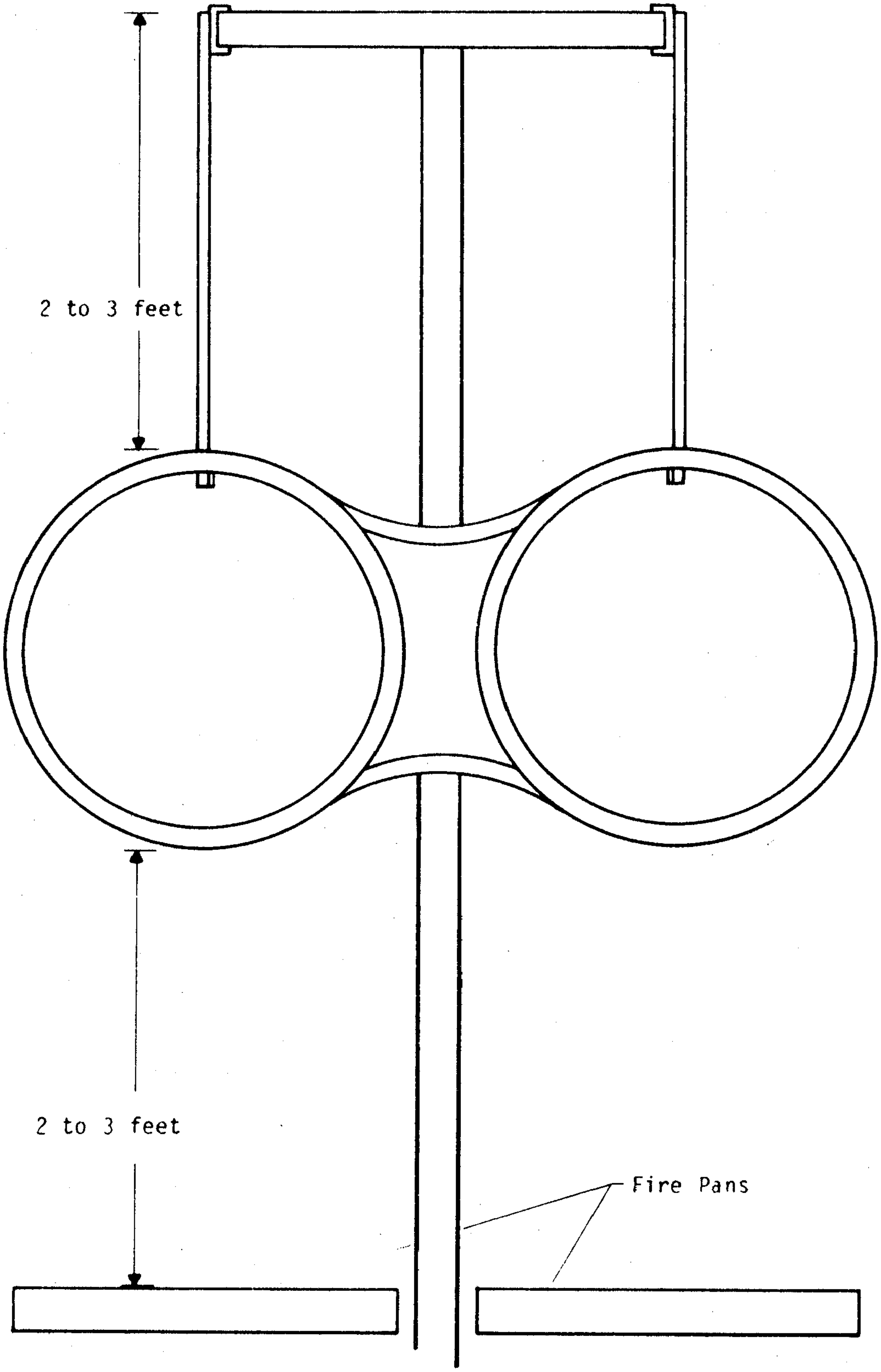


Figure D-9. Fire Pan Placement for Modified Large-Scale Apparatus.

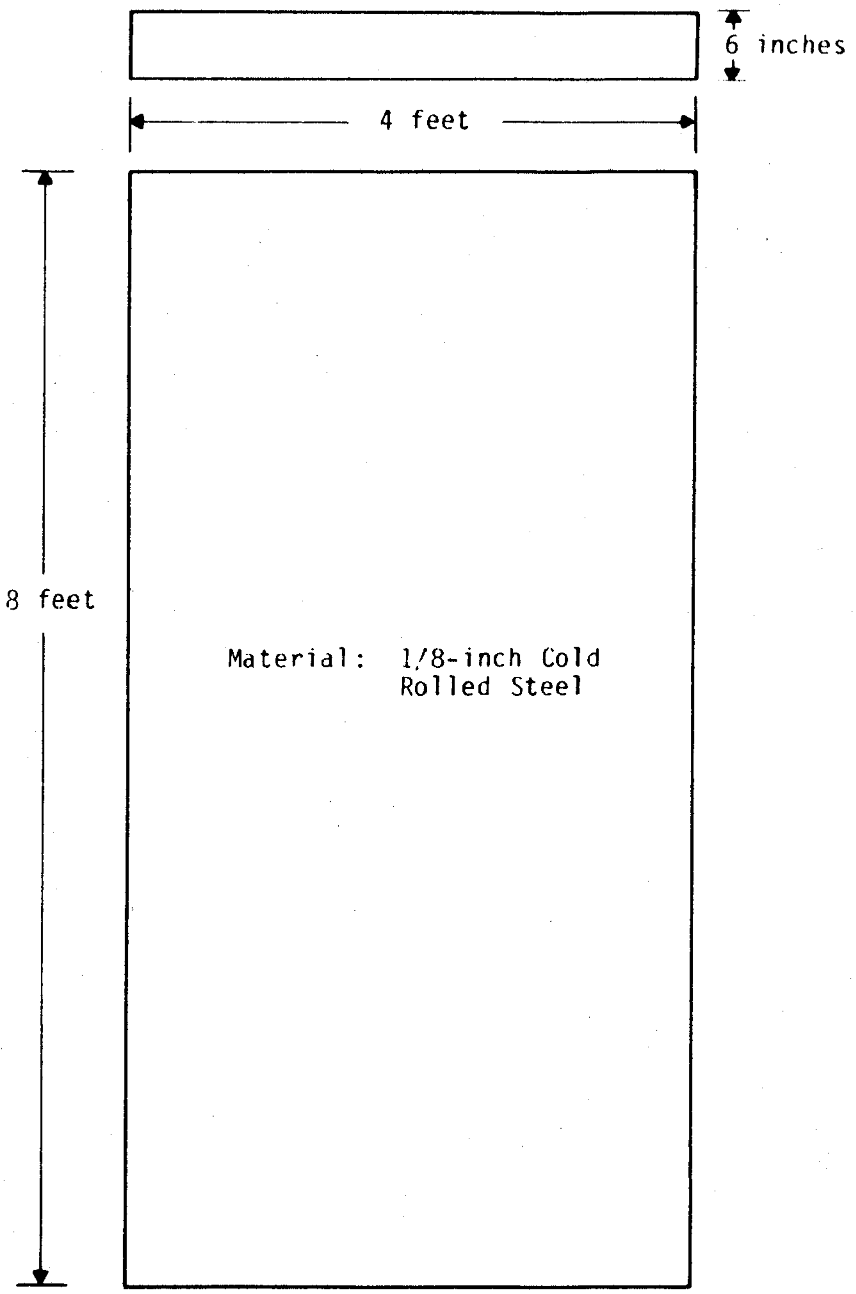


Figure D-10. Fire Pan for Modified Large-Scale Apparatus.

APPENDIX D

SECTION IV

LARGE-SCALE MAGNESIUM FIREFIGHTING PROCEDURE

MAIN FIREFIGHTING UNIT

1. Metal X

The firefighter will apply agent continuously until fire is either extinguished or completely smothered.

The unit to be used will be in a 10-gallon CB (fireguard)-type extinguisher. It will be powered by a nitrogen regulator/valve system set at 150 lb/in^2. This will provide a flow-through constant pressure/flow system.

A second CB unit full of Metal X will be used if necessary.

2. TMB/Halon 2402

Firefighters will apply agent in long bursts to knock down the fire. The objective is to fight the fire until it is either completely extinguished or reduced to a smoldering fire without unnecessary flooding with excess agent. The test engineer will direct the firefighter as to when to start/stop the agent flow.

Unit to be used will be a 10-gallon CB (fireguard)-type extinguisher. It will be pressurized with nitrogen to 150 lb/in^2. The unit will be used until all agent has been expelled or the fire extinguished.

A 1-inch red "Boston Marathoner" hose connected to a small Akron Brass handle with a Moon variable nozzle will be used.

SECONDARY FIREFIGHTING UNIT

1. H_2O

Metal X Fire--Other firefighters will back up the main firefighter and assist if this firefighter gets into trouble. Otherwise, H_2O will not be applied to the fire until the TMB/Halon application has been completed.

A U.S. Army "water buffalo" (capacity 500 gallons) will be used as a water reservoir. A Teel submersible pump (Model No. 3P621--1/2 hp, 20 gal/min) will be placed in the reservoir and will be connected to a 1-inch red "Boston Marathoner" hose with an Akron Brass marauder (Style 4507) and an in-line 200-lb/in^2 gage attached.

A 7.5-kilowatt (120-240-volt) generator, Overlowe Model No. KP 7500 B 1CB 2E (Serial No. 84-9-8160A) will be used to power the submersible pump. A 100-125-lb/in^2 pressure will be obtained.

The following backup units will be used only if an emergency occurs:

2. DP-13 truck
   - -Halon 1211 system
   - -PKP dry chemical system
3. XP-13 Truck
   - -AFFF Foam System
   - -Halon 1211 System

SAFETY REQUIREMENTS

1. Firefighters will fight the fire only from the upwind side. Fumes from the fire are always to be flowing away from the firefighter.

2. If fire gets uncontrollable, firefighters are instructed to abandon it.

3. Firefighters will be required to wear full silvers.

4. Spectators will be required to stay 75-100 feet away from the fire and will have to wear safety magnesium goggles.

5. During the Metal X fires, firefighters will wear respirators.

6. During the TMB/Halon fires, the main firefighter will wear a SCBA. The backup firefighter will have an SCBA ready for emergency use.

> NOTE: To maintain accuracy of agent application and test repeatability, only one firefighter will apply agent or H_2O to the fire. The backup firefighter will be used only in emergency situations.

(The reverse of this page is blank.)

APPENDIX E
FIELD TEST DATA SHEETS
MEDIUM-SCALE TESTS

FIELD TEST DATA SHEET

TEST TYPE medium-scale, class D

DATE 30 May 1985

TIME OF DAY 11:25 AM

WIND S-SW, 10-15 mph

WEATHER cloudy, windy

FUEL(S) 7 magnesium ingots (500-600 grams each) + magnesium strips

AGENT(S) Boralon-2-10V

NOZZLE(S) 61507 black plastic foam nozzle

EXTINGUISHER TYPE(S) 2-1/2-gallon hand-held

EXTINGUISHER PRESSURE 100 psi

EXTINGUISHER INITIAL WEIGHT(S) 30.5 pounds

EXTINGUISHER FINAL WEIGHT(S) 25.5 pounds

APPLICATION TIME 9 seconds to extinguishment

FLOW RATE 33 pounds/minute

COMMENTS A long time was required to ignite the foam. This was the first test in which a foam nozzle was used to apply a TMB-containing agent.

CONCLUSIONS Foamed TMB appears to give a significantly improved coverage and spray characteristics than does non-foamed TMB.

FIELD TEST DATA SHEET

TEST TYPE medium-scale, class B,D

DATE 30 May 1985

TIME OF DAY 12 noon

WIND S-SW, 10-15 mph

WEATHER cloudy, windy

FUEL(S) five magnesium ingots (400-600 grams each), JP-4 on water

AGENT(S) Boralon-2-10V for magnesium; 6% AFFF for JP-4

NOZZLE(S) Boralon: 61507 black plastic foam nozzle

EXTINGUISHER TYPE(S) Boralon: 2-1/2-gallon hand-held; AFFF: 10-gallon CB

EXTINGUISHER PRESSURE hand-held: 100 psi

EXTINGUISHER INITIAL WEIGHT(S) hand-held: 34 pounds

EXTINGUISHER FINAL WEIGHT(S) hand-held: 30 pounds

APPLICATION TIME Boralon applied for 23 seconds then AFFF

FLOW RATE approximate average for Boralon-2-10V: 11 pounds/minute

COMMENTS Magnesium was "extinguished" first (23 seconds). AFFF was then applied. After extinguishment of liquid fuel, AFFF was applied to the magnesium. A violent reaction made it apparent that magnesium had not been entirely extinguished. This was the first attempt at extinguishing a fire containing both a metal and a liquid fuel. Note: The magnesium was not in actual contact with the JP-4.

CONCLUSIONS JP-4 fires can be extinguished even in the presence of burning magnesium.

FIELD TEST DATA SHEET

TEST TYPE medium-scale, class D

DATE 20 June 1985

TIME OF DAY 8:15 AM

WIND S-SW, 2-3 mph

WEATHER sunny, breezy

FUEL(S) magnesium ingots (1536 grams)

AGENT(S) 3% AFFF, then Halon 2402, then water

NOZZLE(S) Ansul dual-agent foam nozzle

EXTINGUISHER TYPE(S) AFFF: 10-gallon CB

EXTINGUISHER PRESSURE AFFF extinguisher: 150 psi

EXTINGUISHER INITIAL WEIGHT(S) AFFF extinguisher: 330 pounds

EXTINGUISHER FINAL WEIGHT(S)

APPLICATION TIME AFFF: 22 seconds

FLOW RATE

COMMENTS This test was to determine the effect of AFFF on magnesium. AFFF reacted violently (just like water) and caused the magnesium to spray out. Halon 2402 was then applied. Again a violent reaction was observed. Water was then applied. This test was used to obtain baseline information on the reaction of AFFF with magnesium for use in interpreting Class B,D fire test results.

CONCLUSIONS Magnesium reacts with AFFF in the same manner as water.

FIELD TEST DATA SHEET

TEST TYPE medium-scale, class B,D

DATE 20 June 1985

TIME OF DAY 8:50 AM

WIND S-SW, 5 mph

WEATHER sunny, breezy

FUEL(S) magnesium ingots (1957 grams) separated from JP-4 on water

AGENT(S) Boralon-2-10V; 3% AFFF

NOZZLE(S) Ansul dual-agent foam nozzle

EXTINGUISHER TYPE(S) Boralon: 2-1/2 gallon hand-held; AFFF: 10-gallon CB

EXTINGUISHER PRESSURE hand-held: 100 psi; CB: 150 psi

EXTINGUISHER INITIAL WEIGHT(S) hand-held: 25 pounds

EXTINGUISHER FINAL WEIGHT(S) hand-held: 17 pounds

APPLICATION TIME AFFF: 13 sec. total (2 applications); Boralon: 13 sec.

FLOW RATE Boralon-2-10V: 37 pounds/minute

COMMENTS The magnesium was elevated above the JP-4 by fire bricks. The magnesium was ignited first, then JP-4 was pumped in. 3% AFFF was used first to extinguish the liquid-fuel fire. Boralon-2-10V was then applied to the magnesium. This blew the cover off the JP-4 allowing it to reignite. A second application of AFFF extinguished the liquid-fuel fire.

CONCLUSIONS There is no evidence of incompatibility between AFFF and Boralon-2-10V; however, one must be careful not to blow the foam off an extinguished Class B fire when applying a TMB agent.

FIELD TEST DATA SHEET

TEST TYPE medium-scale, class B,D

DATE 20 June 1985

TIME OF DAY 9:15 AM

WIND S-SW, 3-5 mph

WEATHER sunny, breezy

FUEL(S) magnesium ingots (approx. 2 kg), JP-4 in contact with each other

AGENT(S) 3% AFFF; Boralon-2-10V

NOZZLE(S) Ansul dual-agent foam nozzle

EXTINGUISHER TYPE(S) Boralon: 2-1/2-gallon hand-held; AFFF: 10-gallon CB

EXTINGUISHER PRESSURE CB: 150 psi; hand-held: 100 psi

EXTINGUISHER INITIAL WEIGHT(S) hand-held: 31.5 pounds

EXTINGUISHER FINAL WEIGHT(S) hand-held: 19.5 pounds

APPLICATION TIME Boralon-2-10V: 25 seconds

FLOW RATE Boralon-2-10V: 29 pounds/minute

COMMENTS This was the first test in which burning magnesium was in contact with burning JP-4. The magnesium was ignited first, then JP-4 was pumped in. AFFF was applied to the liquid fuel; however, it was used up. Boralon-2-10V was then applied to the magnesium. Halon 2402 was applied to the liquid fuel; however, it was too hot for the halon. Cooled with water; final extinguishment with halon.

CONCLUSIONS This was a complicated large fire. A mistake was made in having too little foam. Halon works poorly on mixed B,D fires because it does not blanket the fuel (which continues to reignite from the hot metal).

FIELD TEST DATA SHEET

TEST TYPE medium-scale, class D

DATE 21 June 1985

TIME OF DAY 8:45 AM

WIND calm

WEATHER sunny

FUEL(S) magnesium ingots (1961 grams)

AGENT(S) 2-1/2 gallons of 3% AFFF with approximately 5 pounds borax

NOZZLE(S) black plastic foam nozzle

EXTINGUISHER TYPE(S) 2-1/2-gallon hand-held

EXTINGUISHER PRESSURE 100 psi

EXTINGUISHER INITIAL WEIGHT(S) 24 pounds

EXTINGUISHER FINAL WEIGHT(S) 8 pounds

APPLICATION TIME 59 seconds

FLOW RATE 16 pounds/minute

COMMENTS Magnesium was on bricks. The mixture failed to extinguish the and actually appeared to aggravate it more than plain water. This test was conducted to test an agent similar to one on which Mine Safety Appliance Research had worked on at one time.

CONCLUSIONS AFFF with this amount of borax is an unacceptable agent. This test should be repeated with the AFFF solution saturated with borax.

FIELD TEST DATA SHEET

TEST TYPE medium-scale, class B,D

DATE 21 June 1985

TIME OF DAY 9:10 AM

WIND S-SW, 1-2 mph

WEATHER sunny

FUEL(S) magnesium ingots (1879 g) in contact with JP-4

AGENT(S) 3% AFFF foam on JP-4; Boralon-2-10V on magnesium

NOZZLE(S) AFFF: XP-13 foam nozzle; Boralon-2-10V: black plastic foam nozzle

EXTINGUISHER TYPE(S) AFFF: 10-gallon CB; Boralon: 2-1/2-gallon hand-held

EXTINGUISHER PRESSURE CB: 150 psi; hand-held: 100 psi

EXTINGUISHER INITIAL WEIGHT(S) hand-held: 24 pounds

EXTINGUISHER FINAL WEIGHT(S) hand-held: 20 pounds

APPLICATION TIME AFFF: 31 seconds; Boralon: 9 seconds

FLOW RATE Boralon-2-10V: 27 pounds/minute

COMMENTS This is the first successful test (and only the second test run) with burning magnesium and burning JP-4 in contact. The JP-4 fire was first extinguished with AFFF, then the magnesium fire was extinguished with Boralon-2-10V. The residues were cooled with water. At the start of the fire it was impossible to see the burning magnesium owing to the burning fuel. A typical scenario.

CONCLUSIONS A mixed-fuel magnesium/JP-4 fire can be successfully extinguished applying AFFF first to extinguish the liquid-fuel fire and then applying the Class D agent. That the magnesium was in contact with the JP-4 made this test very difficult.

FIELD TEST DATA SHEET

TEST TYPE medium-scale, class B,D

DATE 18 July 1985

TIME OF DAY 2:10 PM

WIND S-SW, 5 mph

WEATHER cloudy

FUEL(S) magnesium squares from sheet stock (2076 grams) with JP-4

AGENT(S) 10 gallons 3% AFFF with 30-40 pounds sodium metaborate (saturated)

NOZZLE(S) XP-13 foam nozzle

EXTINGUISHER TYPE(S) 10-gallon CB

EXTINGUISHER PRESSURE 150 psi

EXTINGUISHER INITIAL WEIGHT(S) 35 pounds

EXTINGUISHER FINAL WEIGHT(S)

APPLICATION TIME

FLOW RATE

COMMENTS This test was meant to test AFFF saturated with a borate salt. Sodium metaborate was used owing to its large solubility. The fire was large and hot. Application of lots of foam from about 15 feet away seemed to extinguish both the JP-4 fire and the magnesium fire; however, the magnesium continued to burn under the foam blanket.

CONCLUSIONS Though copious amounts of AFFF/borate foam may extinguish fires containing both a liquid fuel and magnesium, the addition of borate appears to harm the Class B capability of AFFF. Need to examine this agent further.

FIELD TEST DATA SHEET

TEST TYPE medium-scale, class B,D

DATE 18 July 1985

TIME OF DAY

WIND calm

WEATHER partly cloudy

FUEL(S) magnesium ingots (2011 grams); JP-4

AGENT(S) 3% AFFF saturated with sodium metaborate (see preceding)

NOZZLE(S) XP-13 foam nozzle

EXTINGUISHER TYPE(S) 10-gallon CB

EXTINGUISHER PRESSURE 150 psi

EXTINGUISHER INITIAL WEIGHT(S)

EXTINGUISHER FINAL WEIGHT(S)

APPLICATION TIME

FLOW RATE

COMMENTS This was a repeat of the preceding test. Ran out of foam during test. Attempt to use Boralon-2-10V failed when extinguisher stuck. Halon 1211 from a small hand-held extinguisher proved incapable of handling the large, intense fire. Water was finally used to cool and extinguish the fire.

CONCLUSIONS Test was invalid owing to multiple extinguishant problems. Still need to look further at AFFF saturated with a borate.

FIELD TEST DATA SHEET

TEST TYPE medium-scale, class D

DATE 23 July 1985

TIME OF DAY 10:30 AM

WIND calm

WEATHER sunny to partly cloudy

FUEL(S) magnesium square plate scrap (approximately 2000 grams)

AGENT(S) 10 gallons AFFF with 20 pounds sodium metaborate

NOZZLE(S) XP-13 foam nozzle

EXTINGUISHER TYPE(S) 10-gallon CB

EXTINGUISHER PRESSURE 150 psi

EXTINGUISHER INITIAL WEIGHT(S) 328.5 pounds

EXTINGUISHER FINAL WEIGHT(S) 263 pounds

APPLICATION TIME

FLOW RATE

COMMENTS Initially the foam intensified the fire and made it explode and scatter; however, there was no sparking unlike that usually observed with AFFF. Did extinguish.

CONCLUSIONS AFFF saturated with borate appears marginally promising but the testing needs to be repeated.

FIELD TEST DATA SHEET

TEST TYPE medium-scale, class D

DATE 23 July 1985

TIME OF DAY PM

WIND S-SW, 1-2 mph

WEATHER sunny to partly cloudy

FUEL(S) magnesium (2000 grams)

AGENT(S) 6 % AFFF with sodium metaborate (agent remaining from last test)

NOZZLE(S) XP-13 foam nozzle

EXTINGUISHER TYPE(S) 10-gallon CB

EXTINGUISHER PRESSURE 150 psi

EXTINGUISHER INITIAL WEIGHT(S) 264 pounds

EXTINGUISHER FINAL WEIGHT(S)

APPLICATION TIME

FLOW RATE

COMMENTS This test was initially meant to be a Class B,D fire test; however, the pump for the JP-4 failed to operate properly. The AFFF/borate agent remaining from the preceding test was dumped on the magnesium, emptying the CB tank. There was a large amount of sparking.

CONCLUSIONS AFFF saturated with borate does not look promising.

FIELD TEST DATA SHEET

TEST TYPE medium-scale, class B,D

DATE 23 July 1985

TIME OF DAY 1:45 PM

WIND W, 3-4 mph

WEATHER sunny to partly cloudy

FUEL(S) 1976 grams magnesium; JP-4

AGENT(S) 5 gallons 6% AFFF with 64 pounds sodium metaborate

NOZZLE(S) XP-13 foam nozzle

EXTINGUISHER TYPE(S) 10-gallon CB

EXTINGUISHER PRESSURE 150 psi

EXTINGUISHER INITIAL WEIGHT(S) 356.5 pounds

EXTINGUISHER FINAL WEIGHT(S) 233.5 pounds

APPLICATION TIME

FLOW RATE

COMMENTS The magnesium was ignited and the AFFF/borate foam was added. The magnesium sparked and scattered. JP-4 was added, the fire intensified, and the magnesium sparked. The remainder of the foam was applied but failed to extinguish the fire. The residue was finally extinguished by cooling with water.

CONCLUSIONS AFFF/borax is unacceptable as a Class D agent.

FIELD TEST DATA SHEET

TEST TYPE medium-scale, class D

DATE 31 July 1985

TIME OF DAY 1:50 PM

WIND S-SW, 5 mph

WEATHER breezy, partly cloudy

FUEL(S) magnesium square plate stock (2000 grams)

AGENT(S) Boralon-1-10V

NOZZLE(S) black plastic foam nozzle

EXTINGUISHER TYPE(S) 2-1/2-gallon hand-held

EXTINGUISHER PRESSURE 100 psi

EXTINGUISHER INITIAL WEIGHT(S) 33.1 pounds

EXTINGUISHER FINAL WEIGHT(S) 28.7 pounds

APPLICATION TIME 9 seconds

FLOW RATE 29 pounds/minute

COMMENTS This was the first test with a mixture of TMB and Halon 1211. The Extinguishment was very rapid. There was good coverage.

CONCLUSIONS 90% TMB/10% Halon 1211 (Boralon-1-10V) appears very promising as a Class D agent. The extinguishing ability appears at least as good as that of Boralon-2-10V.

FIELD TEST DATA SHEET

TEST TYPE medium-scale, class D

DATE 31 July 1985

TIME OF DAY 2:15 PM

WIND S-SW, 1-2 mph

WEATHER sunny, breezy

FUEL(S) magnesium scrap blocks (2000 grams)

AGENT(S) Boralon-1-10V

NOZZLE(S) black plastic foam nozzle

EXTINGUISHER TYPE(S) 2-1/2-gallon hand-held

EXTINGUISHER PRESSURE 100 psi

EXTINGUISHER INITIAL WEIGHT(S) 28.8 pounds

EXTINGUISHER FINAL WEIGHT(S) 24.9 pounds

APPLICATION TIME 7 seconds

FLOW RATE 33 pounds/minute

COMMENTS Very fast extinguishment.

CONCLUSIONS Boralon-1-10V exhibits excellent extinguishing ability, probably better than that of Boralon-2-10V.

FIELD TEST DATA SHEET

TEST TYPE medium-scale, class D

DATE 1 August 1985

TIME OF DAY 2:00 PM

WIND calm

WEATHER sunny to partly cloudy

FUEL(S) magnesium (2000 grams)

AGENT(S) Boralon-1-20V

NOZZLE(S) black plastic foam nozzle

EXTINGUISHER TYPE(S) 2-1/2-gallon hand-held

EXTINGUISHER PRESSURE 100 psi

EXTINGUISHER INITIAL WEIGHT(S) 35.9 pounds

EXTINGUISHER FINAL WEIGHT(S) 31.0 pounds

APPLICATION TIME

FLOW RATE

COMMENTS This is the first in a series to determine the maximum (optimum?) amount of Halon 1211 which can be put into Boralon-1. Obtained excellent extinguishment with no sparking. Some secondary fire still present.

CONCLUSIONS Boralon-1-20V extinguishes magnesium well in a medium-scale test. 20 percent Halon 1211 causes no problems with magnesium reactivity.

FIELD TEST DATA SHEET

TEST TYPE medium-scale, class D

DATE 1 August 1985

TIME OF DAY 2:40 PM

WIND calm

WEATHER sunny to partly cloudy

FUEL(S) magnesium (2000 grams)

AGENT(S) Boralon-1-20V

NOZZLE(S) black plastic foam nozzle

EXTINGUISHER TYPE(S) 2-1/2-gallon hand-held

EXTINGUISHER PRESSURE 100 psi

EXTINGUISHER INITIAL WEIGHT(S) 31.0 pounds

EXTINGUISHER FINAL WEIGHT(S)

APPLICATION TIME 9 seconds

FLOW RATE

COMMENTS This is a duplicate of the preceding test. The results were the same. Good extinguishment with some secondary fire. No sparking was observed.

CONCLUSIONS Boralon-1-20V appears to be an excellent agent. Overall it appears better than Boralon-2-10V.

FIELD TEST DATA SHEET

TEST TYPE medium-scale, class D

DATE 2 August 1985

TIME OF DAY 12:24 PM

WIND S-SW, 1 mph

WEATHER cloudy, rainy

FUEL(S) magnesium (2009 grams)

AGENT(S) Boralon-1-30V

NOZZLE(S) black plastic foam nozzle

EXTINGUISHER TYPE(S) 2-1/2-gallon hand-held

EXTINGUISHER PRESSURE 100 psi

EXTINGUISHER INITIAL WEIGHT(S) 36.1 pounds

EXTINGUISHER FINAL WEIGHT(S) 32.1 pounds

APPLICATION TIME 7 seconds

FLOW RATE 34 pounds/minute

COMMENTS Applied in a continuous stream. Good extinguishment with some slight sparking. Secondary fire essentially nonexistent. Large halon cloud.

CONCLUSIONS 30% Halon 1211 may cause some reactivity problem; however, sparking is very slight. This agent is very good for its secondary fire characteristics.

FIELD TEST DATA SHEET

TEST TYPE medium-scale, class D

DATE 2 August 1985

TIME OF DAY 12:45 PM

WIND W, 2 mph

WEATHER cloudy, rainy

FUEL(S) magnesium (2000 grams)

AGENT(S) Boralon-1-30V

NOZZLE(S) black plastic foam nozzle

EXTINGUISHER TYPE(S) 2-1/2-gallon hand-held

EXTINGUISHER PRESSURE 100 psi

EXTINGUISHER INITIAL WEIGHT(S) 31.8 pounds

EXTINGUISHER FINAL WEIGHT(S) 28.0 pounds

APPLICATION TIME

FLOW RATE

COMMENTS Agent was applied in bursts rather than continuously. Very good coating was obtained. No sparking was observed.

CONCLUSIONS Boralon-1-30V appears excellent, particularly when applied discontinuously. This time there appeared to be no indication of reactivity with hot magnesium.

FIELD TEST DATA SHEET

TEST TYPE medium-scale, class D

DATE 2 August 1985

TIME OF DAY 2:20 PM

WIND calm

WEATHER cloudy, rainy

FUEL(S) magnesium (2000 grams)

AGENT(S) Boralon-1-40V

NOZZLE(S) black plastic foam nozzle

EXTINGUISHER TYPE(S) 2-1/2-gallon hand-held

EXTINGUISHER PRESSURE 100 psi

EXTINGUISHER INITIAL WEIGHT(S) 37.4 pounds

EXTINGUISHER FINAL WEIGHT(S) 33.8 pounds

APPLICATION TIME 6 seconds

FLOW RATE 36 pounds/minute

COMMENTS This agent contains the most Halon 1211 yet used with TMB. The agent was applied continuously. There was some slight sparking.

CONCLUSIONS 40% Halon 1211 in TMB may cause some reactivity problems. Extinguishment still looks good.

FIELD TEST DATA SHEET

TEST TYPE medium-scale, class D

DATE 2 August 1985

TIME OF DAY 2:45 PM

WIND calm

WEATHER cloudy, rainy

FUEL(S) magnesium (2000 grams)

AGENT(S) Boralon-1-40V

NOZZLE(S) black plastic foam nozzle

EXTINGUISHER TYPE(S) 2-1/2-gallon hand-held

EXTINGUISHER PRESSURE 100 psi

EXTINGUISHER INITIAL WEIGHT(S) 33.8 pounds

EXTINGUISHER FINAL WEIGHT(S) 29.5 pounds

APPLICATION TIME

FLOW RATE

COMMENTS Agent was applied in spurts. A lot of sparking occurred.

CONCLUSIONS 40% Halon 1211 in the TMB appears to give excessive reactivity toward the magnesium. Boralon-1-30V may be optimal as far as reactivity is concerned.

FIELD TEST DATA SHEET

TEST TYPE medium-scale, class B

DATE 19 August 1985

TIME OF DAY 3:00 PM

WIND calm

WEATHER partly cloudy

FUEL(S) JP-4 only

AGENT(S) Boralon-1-30V

NOZZLE(S) straight flow-through cone

EXTINGUISHER TYPE(S) 2-1/2-gallon hand-held

EXTINGUISHER PRESSURE 100 psi

EXTINGUISHER INITIAL WEIGHT(S) 36 pounds

EXTINGUISHER FINAL WEIGHT(S) 16.5 pounds

APPLICATION TIME

FLOW RATE

COMMENTS This test was conducted to determine whether high loading of TMB with Halon 1211 might give an agent with some Class B fire extinguishment capabilities. Boralon-1-30V failed to extinguish the fire. The fire was finally extinguished with Halon 1211.

CONCLUSIONS Boralon-1-30V is an unacceptable agent for JP-4 fires.

FIELD TEST DATA SHEET

TEST TYPE medium-scale, class B

DATE 19 August 1985

TIME OF DAY 3:15 PM

WIND S, 1 mph

WEATHER partly cloudy

FUEL(S) JP-5 only

AGENT(S) Boralon-1-30V

NOZZLE(S) straight flow-through cone

EXTINGUISHER TYPE(S) 2-1/2-gallon hand-held

EXTINGUISHER PRESSURE 100 psi

EXTINGUISHER INITIAL WEIGHT(S) 36.5 pounds

EXTINGUISHER FINAL WEIGHT(S)

APPLICATION TIME

FLOW RATE

COMMENTS This was a test to determine whether a JP-5 fire could be extinguished with Boralon-1-30V alone. The fire could not be extinguished with this agent. Halon 1211 was used to extinguish the fire.

CONCLUSIONS Boralon-1-30V is not a Class B agent.

FIELD TEST DATA SHEET

TEST TYPE medium-scale, class B,D

DATE 21 August 1985

TIME OF DAY 8:45 AM

WIND calm

WEATHER sunny

FUEL(S) magnesium (2050 grams), JP-5

AGENT(S) Boralon-1-30V on magnesium; 6% AFFF foam on JP-5

NOZZLE(S) Boralon: straight flow-through cone; AFFF: XP-13 foam nozzle

EXTINGUISHER TYPE(S) Boralon: 2-1/2-gallon hand-held; AFFF: 10-gallon CB

EXTINGUISHER PRESSURE hand-held: 100 psi; CB: 150 psi

EXTINGUISHER INITIAL WEIGHT(S) hand-held: 36 pounds; CB: 387 pounds

EXTINGUISHER FINAL WEIGHT(S) hand-held: 32.5 pounds; CB: 353 pounds

APPLICATION TIME

FLOW RATE

COMMENTS The JP-5 fire was knocked down first with AFFF foam. The magnesium reacted with the foam. Boralon-1-30V was then applied to the magnesium. Both types of fire were then hit simultaneously with the two agents. The fires were fairly well extinguished by this method. The JP-5 fire was much less intense than the average JP-4 fire.

CONCLUSIONS Simultaneous application of class B and D agents may permit extinguishment of mixed-fuel fires; however, the technique is a little difficult to master.

FIELD TEST DATA SHEET

TEST TYPE medium-scale, class B,D

DATE 21 August 1985

TIME OF DAY 9:15 AM

WIND calm

WEATHER sunny

FUEL(S) magnesium (2000 grams), JP-4

AGENT(S) Boralon-1-30V on magnesium; 6% AFFF foam on JP-4

NOZZLE(S) Boralon: straight flow-through cone; AFFF: XP-13 foam nozzle

EXTINGUISHER TYPE(S) Boralon: 2-1/2-gallon hand-held; AFFF: 10-gallon CB

EXTINGUISHER PRESSURE hand-held: 100 psi; CB: 150 psi

EXTINGUISHER INITIAL WEIGHT(S) hand-held: 33 pounds; CB: 354 pounds

EXTINGUISHER FINAL WEIGHT(S) hand-held: 24 pounds; CB: 298 pounds

APPLICATION TIME

FLOW RATE

COMMENTS The JP-4 fire was knocked down with the AFFF. The magnesium reacted with the foam and some flew out of the pan. The Boralon agent was immediately applied to the magnesium. The fire was extinguished efficiently.

CONCLUSIONS Application of Foam and Boralon in close sequence can effectively extinguish mixed-fuel fires.

FIELD TEST DATA SHEET

TEST TYPE medium-scale, class B,D

DATE 23 August 1985

TIME OF DAY 10:00 AM

WIND calm

WEATHER sunny

FUEL(S) magnesium (857 g); titanium (844 g); aluminum (735 g); JP-4

AGENT(S) Boralon-1-30V on metals; 6% AFFF foam on JP-4

NOZZLE(S) Boralon: straight flow-through cone; AFFF: XP-13 foam nozzle

EXTINGUISHER TYPE(S) Boralon: 2-1/2-gallon hand-held; AFFF: 10-gallon CB

EXTINGUISHER PRESSURE hand-held: 100 psi; CB: 150 psi

EXTINGUISHER INITIAL WEIGHT(S) hand-held: 37 pounds; CB: 397 pounds

EXTINGUISHER FINAL WEIGHT(S) hand-held: 30.5 pounds; CB: 325 pounds

APPLICATION TIME

FLOW RATE

COMMENTS Propane torch would not ignite titanium though some may have burned from close proximity of magnesium. The Boralon-1-30V was applied to the metal fire at the same time that the AFFF foam was applied to the liquid-fuel fire by two fire fighters operating independent delivery systems. The fire was effectively extinguished.

CONCLUSIONS Fires containing mixed-metals with JP-4 fuel can be extinguished effectively by simultaneous application of Boralon-1-30V and AFFF foam to the appropriate portions of the fire. (Note: There was some doubt about titanium ignition.)

FIELD TEST DATA SHEET

TEST TYPE medium-scale, class B,D

DATE 23 August 1985

TIME OF DAY 10:40 AM

WIND calm

WEATHER sunny

FUEL(S) magnesium (710 g); titanium (600 g); aluminum (750 g); JP-5

AGENT(S) Boralon-1-30V on metals; 6% AFFF foam on JP-5

NOZZLE(S) Boralon: straight flow-through cone; AFFF: XP-13 foam nozzle

EXTINGUISHER TYPE(S) Boralon: 2-1/2-gallon hand-held; AFFF: 10-gallon CB

EXTINGUISHER PRESSURE hand-held: 100 psi; CB: 150 psi

EXTINGUISHER INITIAL WEIGHT(S) hand-held: 29.5 pounds; CB: 326 pounds

EXTINGUISHER FINAL WEIGHT(S) hand-held: 24.5 pounds; CB: 268 pounds

APPLICATION TIME

FLOW RATE

COMMENTS The titanium was ignited with an oxyacetylene torch. Both agents were applied simultaneously - the Boralon-1-30V to the metal fire and the AFFF foam to the liquid fuel fire. The agents were applied by separate fire fighters. The foam was applied with too much force and blew liquid fuel off the pan. The fire was extinguished.

CONCLUSIONS Fires containing mixed-metals and JP-5 fuel can be extinguished effectively by simultaneous application of Boralon-1-30V and AFFF foam to the appropriate portions of the fire using two delivery systems operated independently.

FIELD TEST DATA SHEET

TEST TYPE medium-scale, class D

DATE 26 August 1985

TIME OF DAY 2:00 PM

WIND S-SW, 5 mph

WEATHER sunny, hot

FUEL(S) magnesium (2020 grams)

AGENT(S) mixture of 60% TMB, 30% Halon 1211, and 10% Halon 2402 by volume

NOZZLE(S) straight flow-through cone

EXTINGUISHER TYPE(S) 2-1/2-gallon hand-held

EXTINGUISHER PRESSURE 100 psi

EXTINGUISHER INITIAL WEIGHT(S) 36 pounds

EXTINGUISHER FINAL WEIGHT(S) 34.5 pounds

APPLICATION TIME 5 seconds

FLOW RATE approximate average, 18 pounds/minute

COMMENTS Fire extinguished readily but was initially quite small.

CONCLUSIONS The fire was too subdued for a valid test.

FIELD TEST DATA SHEET

TEST TYPE medium-scale, class D

DATE 26 August 1985

TIME OF DAY 2:25 PM

WIND S-SW, 5 mph

WEATHER sunny, hot

FUEL(S) magnesium (2030 grams)

AGENT(S) mixture of 60% TMB, 30% Halon 1211, and 10% Halon 2402 by volume

NOZZLE(S) straight flow-through cone

EXTINGUISHER TYPE(S) 2-1/2-gallon hand-held

EXTINGUISHER PRESSURE 100 psi

EXTINGUISHER INITIAL WEIGHT(S) 35 pounds

EXTINGUISHER FINAL WEIGHT(S) 31.5 pounds

APPLICATION TIME 7 seconds

FLOW RATE 30 gallons/minute

COMMENTS The fire was extinguished; however, there was a violent reaction between the agent and the magnesium. The reaction may have been due to the straight stream applied. A foam nozzle may have been better.

CONCLUSIONS The results indicate that there may be reactivity problems with halon loadings of this magnitude (30 percent Halon 1211 and 10 percent Halon 2402).

FIELD TEST DATA SHEET

TEST TYPE medium-scale, class B,D

DATE 26 August 1985

TIME OF DAY 2:45 PM

WIND S-SW, 5 mph

WEATHER sunny, hot

FUEL(S) magnesium (2043 grams)

AGENT(S) 60% TMB/30% Halon 1211/10% Halon 2402 on magnesium; 6% AFFF on JP-4

NOZZLE(S) TMB agent: straight flow-through cone; AFFF: XP-13 foam nozzle

EXTINGUISHER TYPE(S) TMB agent: 2-1/2-gallon hand-held; AFFF: 10-gallon CB

EXTINGUISHER PRESSURE hand-held: 100 psi; CB: 150 psi

EXTINGUISHER INITIAL WEIGHT(S) hand-held: 32 pounds

EXTINGUISHER FINAL WEIGHT(S) hand-held: 23 pounds

APPLICATION TIME

FLOW RATE

COMMENTS Even with the higher halon loading application of the TMB agent to the JP-4 fire had no effect. Application of the TMB agent to the metal and simultaneous application of the AFFF foam to the liquid-fuel fire was successful in extinguishing fire. This TMB agent did not seem to operate as well as Boralon-1-30V.

CONCLUSIONS A mixture of 60% TMB, 30% Halon 1211, and 10% Halon 2402 by volume does not appear to offer any advantages over Boralon-1-30V and may not be as good. The reactivity toward burning magnesium is higher (see preceding test).

FIELD TEST DATA SHEET

TEST TYPE large-scale, class B,D

DATE 28 August 1985

TIME OF DAY 10:45 AM

WIND S-SW, 5-10 mph

WEATHER sunny, windy

FUEL(S) magnesium (178 pounds); JP-4 (10-20 gallons) floating on water

AGENT(S) Boralon-1-30V on magnesium; 65 AFFF foam on JP-4

NOZZLE(S) Boralon: straight flow-through cone; AFFF: XP-13 foam nozzle

EXTINGUISHER TYPE(S) 10-gallon CB units (both agents)

EXTINGUISHER PRESSURE Boralon: 150 psi held constant; AFFF: 150 psi initial

EXTINGUISHER INITIAL WEIGHT(S) Boralon: 382 pounds; AFFF: 247.5 pounds

EXTINGUISHER FINAL WEIGHT(S) ____

APPLICATION TIME ____

FLOW RATE ____

COMMENTS This was the final field test for Boralon-1-30V prior to the final testing required for Phase IV. This test also served as the shake-down test for the Phase IV mixed-fuel tests. This is the first large-scale mixed class B,D test run on this project. The test went well. Magnesium burned through the cowling and fell into the water, where it was difficult to extinguish.

CONCLUSIONS Application of Boralon-1-30V and AFFF foam from separate extinguishers can successfully extinguish large-scale metal/JP-4 fires. Boralon-1-30V is the agent of choice.

(The reverse of this page is blank.)

APPENDIX F
FIELD TEST DATA SHEETS
LARGE-SCALE TESTS

FIELD TEST DATA SHEET

TEST TYPE large-scale, class B,D

WIND N, 1-3 mph

WEATHER sunny, breezy

FUEL(S) magnesium (163 pounds); JP-4

AGENT(S) Boralon-1-30V on the magnesium; 6% AFFF foam on the JP-4

NOZZLE(S) Boralon: straight flow-through cone; AFFF: XP-13 foam nozzle

EXTINGUISHER TYPE(S) 10-gallon CB tanks for both agents

EXTINGUISHER PRESSURE Boralon: 150 psi constant; AFFF: 150 psi initial

EXTINGUISHER INITIAL WEIGHT(S)

EXTINGUISHER FINAL WEIGHT(S)

APPLICATION TIME

FLOW RATE

COMMENTS JP-4 was ignited in both fire pans. Cowling was totally destroyed. The magnesium burned through and flowed into the water, where it was difficult to extinguish. Application of foam and Boralon-1-30V extinguished the fire, except for a small chunk of burning magnesium which had fallen through the cowling into the water.

CONCLUSIONS Burning magnesium in a pool of water is probably not a scenario. Future tests should not float the fuel.

FIELD TEST DATA SHEET

TEST TYPE large-scale, class B,D   WIND S-SW, 1-2 mph

WEATHER sunny, clear

FUEL(S) Mg (155 pounds), Ti (40 pounds); Al (25 pounds); JP-5

AGENT(S) Boralon-1-30V; 6% AFFF foam

NOZZLE(S) straight flow-through cone; XP-13 foam nozzle

EXTINGUISHER TYPE(S) 10-gallon CB tanks for both agents

EXTINGUISHER PRESSURE 150 psi for both

EXTINGUISHER INITIAL WEIGHT(S) Boralon: 337 pounds; AFFF: 384 pounds

EXTINGUISHER FINAL WEIGHT(S) Boralon: 226 pounds; AFFF: 247 pounds

APPLICATION TIME

FLOW RATE

COMMENTS This test, and the two following tests, were scheduled to practice for a large demonstration before Air Force personnel. practice for a large demonstration involving several Air Force officers. The fire was extremely hot; however, there was little burning of titanium or aluminum. The fire was extinguished with difficulty.

CONCLUSIONS Bursts are more effective than straight streams in extinguishing these fires.

FIELD TEST DATA SHEET

TEST TYPE large-scale, class B,D

WIND N-NE, 5 mph

WEATHER sunny, breezy

FUEL(S) Mg (150 pounds), JP-4

AGENT(S) Boralon-1-30V on magnesium; 6% AFFF foam on JP-4

NOZZLE(S) straight flow-through cone; XP-13 foam nozzle

EXTINGUISHER TYPE(S) 10-gallon CB tanks for both agents

EXTINGUISHER PRESSURE 150 psi for both

EXTINGUISHER INITIAL WEIGHT(S) Boralon: 335 pounds; AFFF: 380 pounds

EXTINGUISHER FINAL WEIGHT(S) Boralon: 253 pounds; AFFF: 277 pounds

APPLICATION TIME

FLOW RATE

COMMENTS This test was scheduled for a demonstration practice. The Boralon-1-30V was applied in bursts of 10-12 seconds. Extinguishment was extremely good.

CONCLUSIONS Bursts are highly effective in combating these fires. Boralon-1-30V with AFFF foam works exceedingly well with these large-scale mixed fuel scenarios.

FIELD TEST DATA SHEET

TEST TYPE large-scale, class B,D

WIND S-SW, 5-10 mph

WEATHER partly cloudy, windy

FUEL(S) Mg (152 pounds), JP-5

AGENT(S) Boralon-1-30V on magnesium; 6% AFFF foam on JP-4

NOZZLE(S) straight flow-through cone; XP-13 foam nozzle

EXTINGUISHER TYPE(S) 10-gallon CB tanks for both agents

EXTINGUISHER PRESSURE 150 psi for both

EXTINGUISHER INITIAL WEIGHT(S) Boralon: 352 pounds; AFFF: 384 pounds

EXTINGUISHER FINAL WEIGHT(S) Boralon: 311 pounds; AFFF: 282 pounds

APPLICATION TIME

FLOW RATE

COMMENTS This test was scheduled for the demonstration. The Boralon-1-30V was applied in bursts. Outstanding extinguishment was obtained. Extremely impressive. Both the JP-5 and the metal fire were extinguished dead.

CONCLUSIONS Boralon-1-30V foam applied in bursts with AFFF foam is an outstanding agent combination for these large-scale mixed-fuel fires.

(The reverse of this page is blank.)

APPENDIX G
PHOTOGRAPHS OF FINAL TESTS

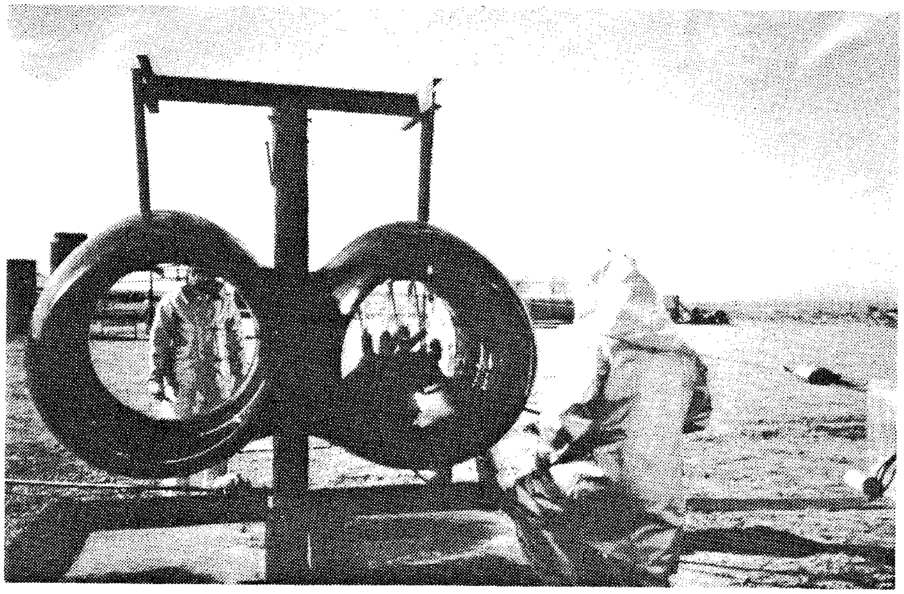


Figure G-1. Metal Loaded into Cowling.

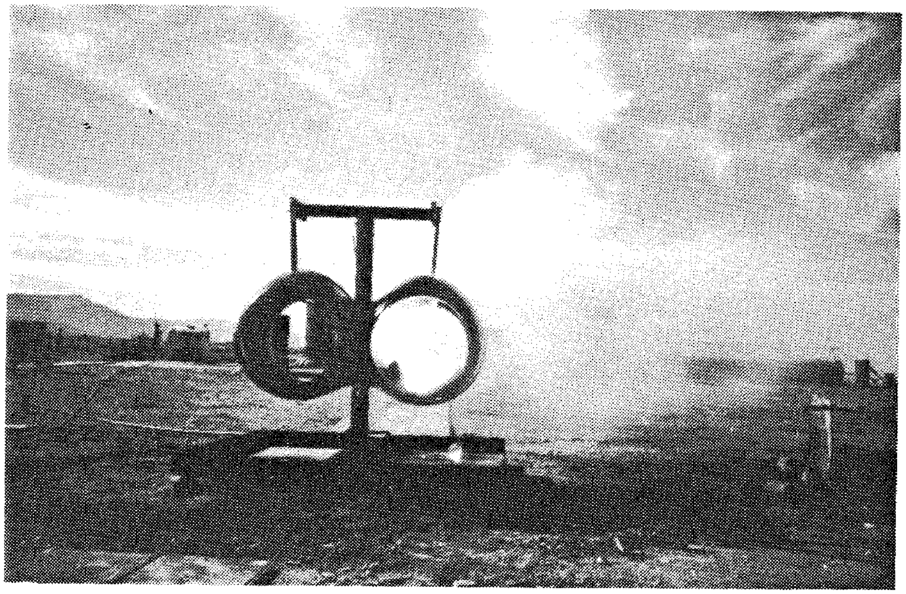


Figure G-2. Metal Ignited in Cowling.

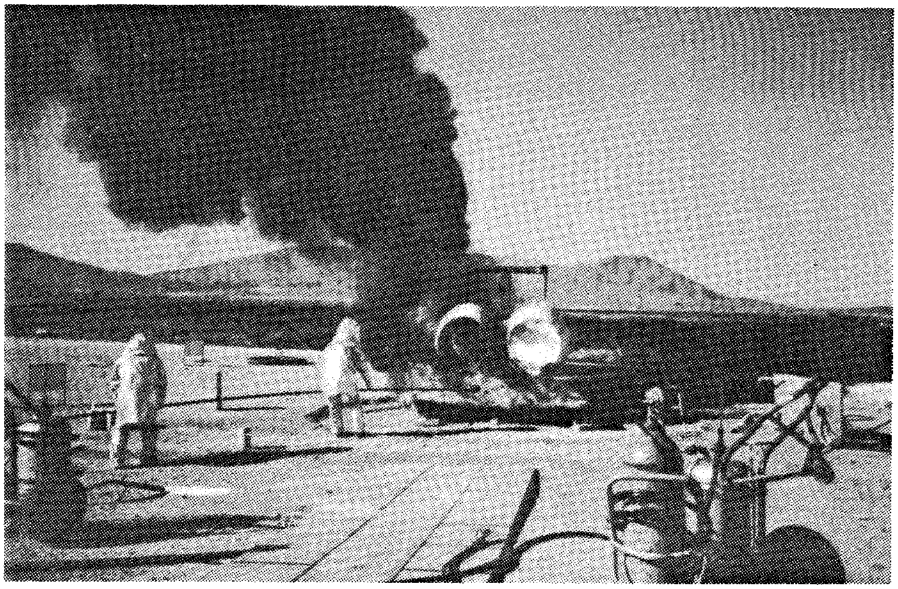


Figure G-3. Jet Fuel Ignited.

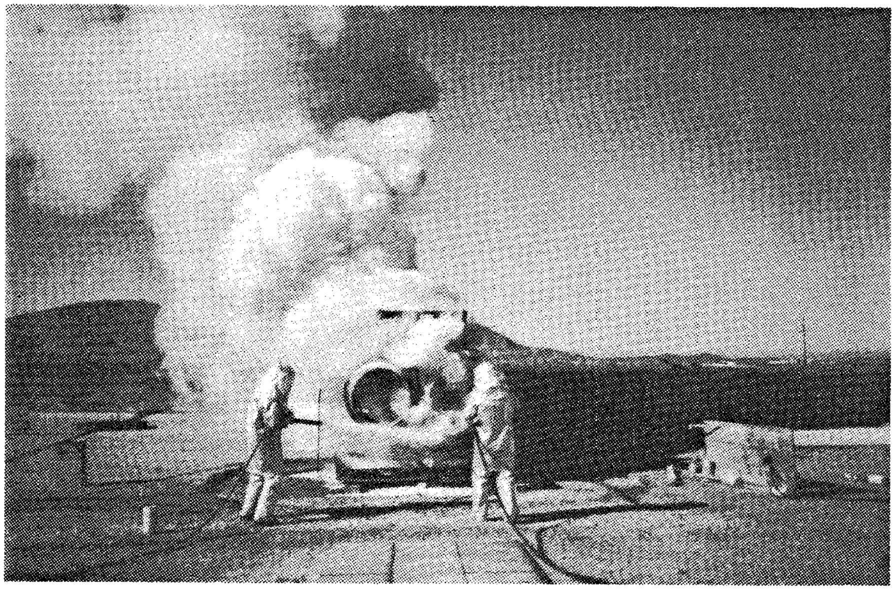


Figure G-4. Application of AFFF Foam and Boralon-1-30V.

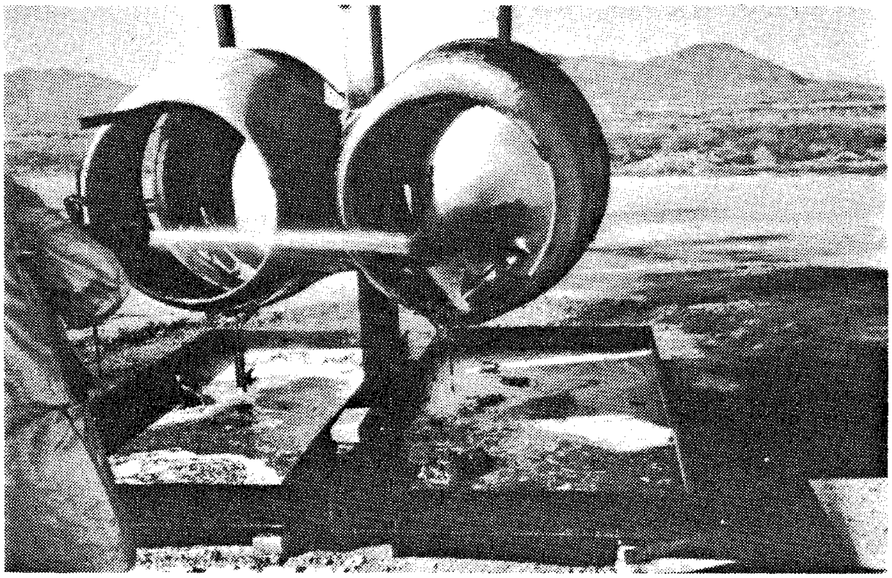


Figure G-5. Cooling Residue with Water Stream.

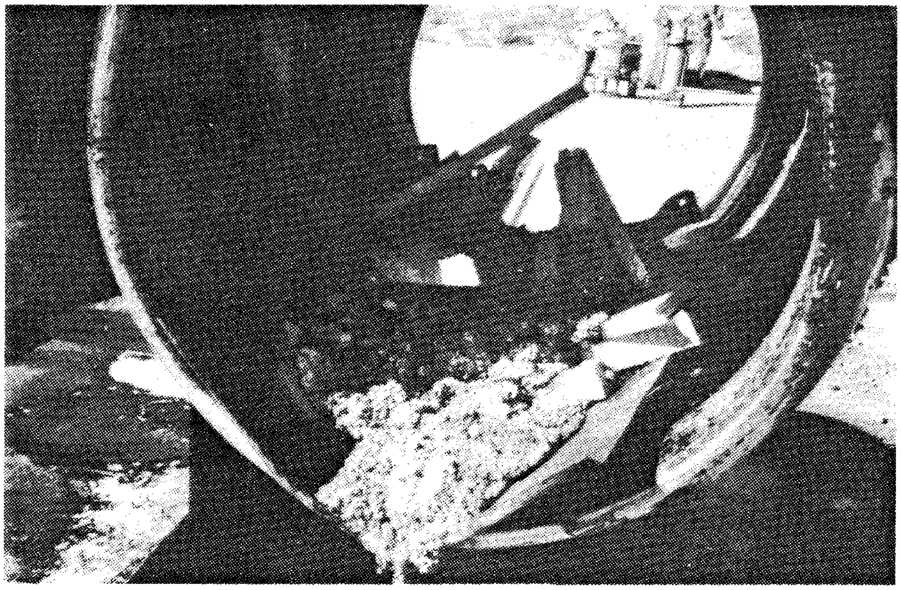


Figure G-6. Residue in Cowling Following Burn.