

THE USE OF TRIMETHOXYBOROXINE FOR THE EXTINGUISHMENT OF METAL FIRES

PART I - MAGNESIUM

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"The Use of Trimethoxyboroxine for the Extinguishment of Metal Fires,
Part 1 - Magnesium," by R. L. Tuve, R. L. Gipe, H. B. Peterson, and R. R.
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Proprietary Powder "A" - - G- 1

Proprietary Powder "B" --- Met-L-X

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ABSTRACT

Magnesium, used effectively in aircraft for landing gear assemblies and other heavy members where strength-weight factors are critical, presents a fire hazard as it is one of the metals which can ignite and burn fiercely. Many magnesium fires causing extensive damage have occurred at air stations as a result of such events as blown out tires and brake seizures. This metal and its alloys present specialized difficulties in fire extinguishment because, when burning, it reacts with water and foam.

Investigation into the above problem has uncovered a new liquid material, trimethoxyboroxine ($(\text{CH}_3\text{O})_3\text{B}\cdot\text{B}_2\text{O}_3$), which was found effective for the control and extinguishment of metal fires, especially fires on magnesium alloys used in aircraft. Small-scale and large-scale model fires have been used to show the superiority of this material over other liquids for the same purpose.

Its efficient "skin" formation on the burning metal, which then allows safe applications of cooling water or foam, its lack of serious toxicity, and its stability in storage are attributes of the material which have led to a recommendation to field-test it in crash fire fighting operations. The material shows a small flare-up when it first hits the burning magnesium, but this is regarded as a minor effect.

Physical properties of trimethoxyboroxine were studied in order to adapt it more efficiently to fire extinguisher use. Attempts to raise the viscosity index by use of methanol additives and the flash point by use of some halogenated hydrocarbon additives proved fruitless. Hydrolysis and gas solubility studies were also carried out. It was concluded that precautions must be taken to protect the liquid from moisture and that air and nitrogen have rather low solubilities in trimethoxyboroxine of about 2.5 ml/liter/1psi.

A portable 2½-gallon stainless-steel stored-pressure extinguisher was developed for initial field fire tests of TMB as a primary extinguishant. This extinguisher has a large neck opening for ease in filling, a removable overfill preventer tube, an easily dismantled valve assembly, a dual-stream lever-operated nozzle, and appropriate gaskets.

PROBLEM STATUS

This is an interim report on the initial phase in the study of trimethoxyboroxine as a metal fire extinguishing agent; work is continuing on this general subject and will be reported in forthcoming issues of this series.

AUTHORIZATION

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**THE USE OF TRIMETHOXYBOROXINE
FOR THE EXTINGUISHMENT OF METAL FIRES
PART 1 - MAGNESIUM**

INTRODUCTION

Magnesium and Its Alloys as Fire Hazards

The use of magnesium and its alloys in equipment requiring relatively high strength and light weight has increased enormously since the discovery of methods for economically winning the metal from sea water. But associated with this increased use as a material of fabrication is an increase in the fire hazard known to exist with magnesium. Exposure of the combustible metal to surroundings where it may reach temperatures capable of initiating its own combustion in air has become more commonplace. As a result, methods of halting such combustion, should it occur, must be developed. The design of aircraft is the most critical field of application of strength-weight factors, and in this application magnesium alloys are exposed to a great number of ignitable materials. Presence of kindling fuel in the form of large quantities of gasoline and oil, sources of ignition in the form of electrical circuits, or local sources of high temperature, and free access to air combine to increase the chances of accidental ignition of the metal. The exposure of personnel to the resulting metal fire is also very likely in the case of aircraft fires and as a consequence the problem is extremely critical.

The high heat conductivity of magnesium and its alloys decreases ignition possibilities when the metal is exposed to a heat source. Thick or bulky castings, such as landing wheels or supporting members, are difficult to ignite because the rapid transfer of heat prevents localized heating to the ignition point. Small parts and thin sheets are more readily ignitable and, because of the greater surface exposed, burn more rapidly and with more violence than do molten pools of metal.

Serious magnesium-alloy fires seem to have occurred most frequently in aircraft which have crash landed, at which time gasoline fires ignited thin sections of the alloy. A large number of less serious fires in aircraft have started when wheel castings ignited from overheating caused by abrasive friction on concrete runways, because of blown out tires, or brake seizures. In most cases where such fires occurred, they were extinguished by the judicious application of water sprays or even dirt.

Once combustion of the metal begins, the process is exothermic, and because of the temperature and reactivity of the burning metal, the use of ordinary extinguishing agents such as water, carbon dioxide, and the halogenated hydrocarbons (such as carbon tetrachloride) results only in an increased rate of reaction. Water and carbon dioxide which are ordinarily inert, react with magnesium at these temperatures adding fuel to the fire in the form of hydrogen and carbon monoxide.

Previous Investigation of Magnesium Fire Extinguishants

The problem of extinguishing metal fires has received sporadic attention at this Laboratory for a number of years. During World War II the difficulties of coping with enemy magnesium incendiary bombs were studied with the general conclusion that such hazards could be partially controlled and final extinguishment achieved only with large

amounts of water in the hands of trained personnel. No completely satisfactory extinguishing agent was available at that time.

The large-scale employment of the alkali metals, such as sodium and potassium, or mixtures of the two, as heat transfer materials in nuclear energy installations reopened the investigations on this problem by this Laboratory and many materials were tested in an effort to obtain a suitable metal-fire extinguishant. This work will be reported in detail at a later date. However, an important outcome of this work was the finding that some inorganic borates were capable of forming impervious glassy coatings under certain conditions. Difficulties in finding nonhygroscopic compounds completely free of water prevented this approach to the problem.

Several investigators (1,2,3) studying extinguishing agents for magnesium fires have published excellent bibliographies on the subject of devices and materials for magnesium fire fighting.

Five principal classes of materials have shown promise as extinguishants for magnesium metal fires. These are:

- (1) Water and water sprays
- (2) Solid, liquid, and gaseous boron and phosphorus compounds
- (3) Liquid, high flash point oils and hydrocarbons
- (4) Solid, high melting point pitches and related organic compounds
- (5) Solid inorganic materials

Mixtures of the above classes have also been used with varying degrees of success.

The use of water and water sprays on various configurations of magnesium fires has been adequately covered by numerous publications (4,5,6). These water processes, when judiciously applied, may be effective cooling and extinguishing methods for these fires.

Proprietary powder "A", a mixture of graphite and an organic phosphate, is currently in wide use in light alloy foundry practice and has yielded good results (4).

Another proprietary material, powder "B", has been employed for some years for extinguishing metal fires. This is a free flowing sodium chloride composition and is forced out of the container by high pressure gas discharge.

An example of the high flash point oil extinguishant is a proprietary product known as Buffalo M-X liquid for magnesium fires. It is forced out of the container by gas pressure and applied to the fire by a long-handled spray-type head controlled by a grip-type valve.

The magnesium extinguishing agents recommended by McCutchan (2) and by Greenstein and Richman (3) are liquids. McCutchan has used a solution of boric acid in triethylene glycol as a quenching and inhibiting agent, and the method of Greenstein and Richman utilizes a mixture of di-isodecyl phthalate in chlorobromomethane to achieve cooling and inhibiting action. No commercial extinguishers using the latter liquids are available as yet.

The chemistry of boron compounds has received a great deal of impetus in the last few years due to the attractive promise of such materials as high-energy fuels. One of the newer compounds available from this program is a liquid addition product of methyl

borate and boric oxide. This new nontoxic, anhydrous liquid, called trimethoxyboroxine (TMB) now shows considerable promise as a magnesium fire extinguishing agent.

Characteristics for an Extinguishant

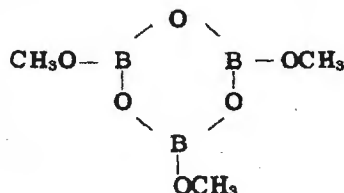
Recently the problem of extinguishing magnesium-alloy fires in ordinary aircraft and in helicopters was reported to be in urgent need of attention by the Bureau of Aeronautics. A preliminary survey of the available commercial materials pointed up the need for a better extinguishing agent with the following characteristics:

- (1) It should be a liquid capable of "throw" into inaccessible areas using normal liquid dispensing methods.
- (2) It must be inherently nontoxic in the native state and form no toxic substances upon pyrolysis during the extinguishment process.
- (3) It should not be flammable to the extent of generating a secondary fire so large in magnitude that other agents are required to combat it.
- (4) It should exert a fire extinguishing or controlling action on the magnesium which will not be cancelled by the successive application of water and foam as cooling and blanketing agents.
- (5) It should be compatible with foam.
- (6) It should be noncorrosive and stable during storage.

THE PROPERTIES OF TRIMETHOXYBOROXINE

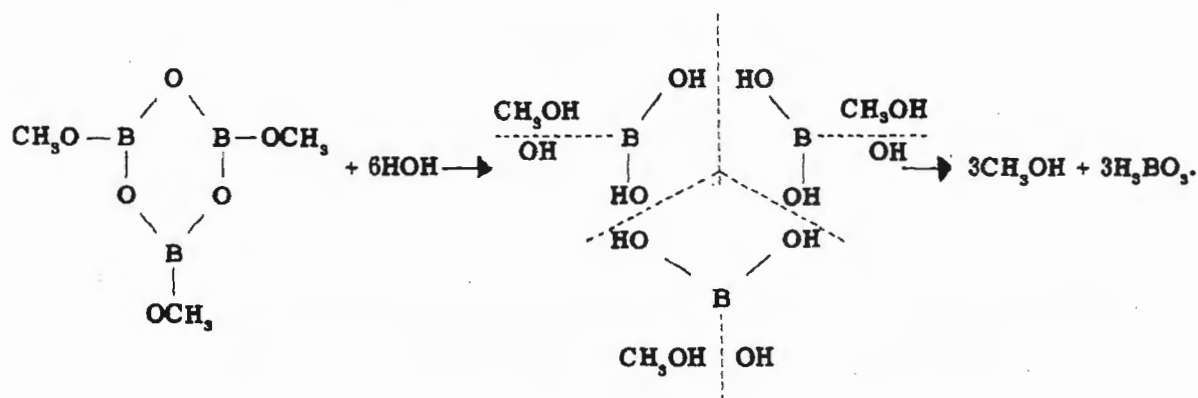
Structure, Method of Preparation, and Physical Properties

Trimethoxyboroxine is a clear, colorless, liquid compound of boron having a molecular weight of 173.6 and is represented by the cyclic structural formula:



The formula may also be represented as $(\text{CH}_3\text{O})_3\text{B} \cdot \text{B}_2\text{O}_3$. The compound is formed by reacting methyl borate with boric oxide (B_2O_3) in an autoclave at 120°C and under a pressure of 60 psi. The reaction can be expressed as: $(\text{CH}_3\text{O})_3\text{B} + \text{B}_2\text{O}_3 \rightarrow (\text{CH}_3\text{O})_3\text{B} \cdot \text{B}_2\text{O}_3$. The reactants appear to be able to combine in a greater ratio than 1:1 and this results in the formation of complex polymers.

TMB reacts readily with water and water vapor to form methanol and orthoboric acid as hydrolytic products (57).

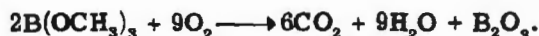


The affinity for water makes it very difficult to handle the material in the laboratory or maintain pure samples for determining physical properties and infrared spectra.

Upon heating, TMB decomposes to boric oxide and methyl borate:



In the presence of oxygen, the methyl borate burns to yield additional boric oxide:



At present the liquid is produced commercially in batch quantities and some of its physical properties may vary from lot to lot. All TMB material used in this experimental project was obtained from the Callery Chemical Co. of Callery, Pennsylvania. The properties of the compound obtained during this investigation appear below.

TYPICAL PHYSICAL PROPERTIES OF TRIMETHOXYBOROXINE

Specific Gravity 20°/20°	1.2125
Surface Tension	24.4 dynes/cm (25°C)
Refractive Index (n_D^{25})	1.3977
Boiling Point	120° - 125°C
Viscosity	13.18 cs (25°C)
Pour Point	-30°C
Flash Point (closed cup)	14° to 18°C
Specific Heat	0.35 cal/C°/gr
Light Transmission (Turbidity)	97 - 98%
% B_2O_3 by analysis	58.7%
Reid Vapor Pressure	1.8 - 2.0 psi (37.8°C)

The methods used in determining the values in the preceding tabulation were standard physical-chemical techniques and ASTM procedures where applicable. In the Reid vapor pressure determination the procedure was modified to omit the addition of water due to its reaction with TMB.

Although a value was observed in a Cottrell boiling point determination, its accuracy is doubtful for two reasons: first, the rate of condensation of the liquid on the stem of the thermometer had greatly influenced the temperature readings, and second, the decomposition temperature is taken to be below the boiling point (7). The material cannot be distilled even when using vacuum distillation techniques (8).

A temperature-viscosity curve is shown as Fig. 1.

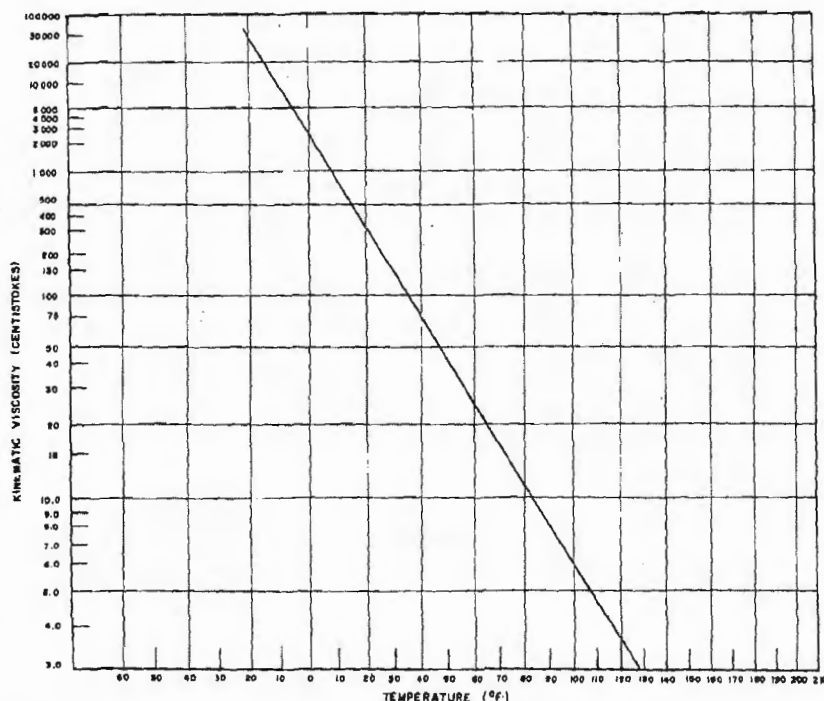


Fig. 1 - TMB temperature-viscosity curve

The flash point determination is also subject to variation because of TMB's unstable nature and extreme susceptibility to hydrolysis. The rate of heating of the sample and the atmospheric humidity have an influence on the observed temperatures because unknown proportions of methanol (flash point 12°C), methyl borate (flash point -2°C), and TMB are present over the sample. The value presented in the tabulation approaches closely the flash point of methanol and should be recognized as the flash point temperature when handling the material under normal atmospheric conditions.

The specific heat was determined by adding heat to the liquid and measuring its rise in temperature, as described in (9). Briefly, the apparatus consisted of a Dewar flask which contained a stirrer and heating element that were suspended in the liquid sample in the calorimeter. The time of the known heat application was measured and the temperature of the liquid was observed. From an average of the tests the specific

heat was calculated to be 0.35 cal/°C/gr. The heat of vaporization of the liquid could not be determined because of its instability.

The boric oxide content of the liquid was determined by titrating the complex acid formed between boric acid and mannitol with 0.1 N solution of sodium hydroxide (10).

The turbidity of TMB was determined by subjecting a sample contained in a cell to a light source and comparing the transmission with that of a similar cell containing distilled water. Trimethoxyboroxine is a clear, colorless liquid, however the light transmitted is always slightly less than that of distilled water. This test indicates the presence of suspended crystals of boric acid resulting from hydrolysis of the liquid.

The solubility of trimethoxyboroxine was determined in a number of common organic solvents. The compound appears to be soluble in ether, ethanol, acetone, xylene, toluene, carbon tetrachloride, carbon disulfide, methanol, and chloroform. It is not soluble in saturated organic solvents such as hexane, cyclohexane, and heptane.

Thermal Decomposition of Trimethoxyboroxine

The thermal characteristics of TMB were studied by slowly dropping 5-ml samples onto the surface of a cast-iron slab whose temperature was maintained constant at each of the 50-degree steps between 50°C and 650°C and noting the resultant formations.

From 50° to 200°C, white fumes, presumably composed of boric acid crystals, rose from the surface of the viscous liquid. The volume of the fumes increased with temperature but appeared to be given off over a shorter period of time. The liquid did not spread evenly over the hot surface at 50°, but collected directly below the point of application. At 100° to 200° the liquid spread more evenly over the surface, leaving a few bare spots. A tight membrane formed over the liquid surface, which resulted from the breakdown of the compound. The residual material (after decomposition) was very viscous while hot, and solidified upon cooling.

At 250°C, the white vapors evolved from the liquid at such a high rate that large bubbles formed in the liquid, which would expand and collapse, leaving a large cavity in the tacky liquid of trimethoxyboroxine.

At 400°, when a flame was brought in contact with the vapors which were being evolved, the flame flashed back to the surface where escaping gases continued to burn with the characteristic green-colored flame of boron. The burning on the surface resulted in the formation of a brittle, blackish-gray crust. When no surface burning occurred, no crust formed.

At 500° and above there was an autoignition of vapor when the TMB was dropped onto the heated surface. The flash resulted in the vapors burning on the surface, which again caused the formation of a crust over the surface.

STUDIES OF THE OXIDATION AND IGNITION OF MAGNESIUM AND DOWMETAL "C"

References (11) and (12) have reported in considerable detail laboratory studies of the oxidation and ignition temperatures of magnesium and its alloys under many conditions such as in oxygen at reduced and elevated pressures and in mixtures of SO₂ and O₂, and H₂ and O₂. Both papers note the formation of the black coating immediately prior to ignition. Leontis and Rhines (11) analyzed the material by x-ray and diffraction analysis and report it to be MgO, its color deviation from the usual white being caused by deficiency

of magnesium or oxygen atoms. Combustion is explained as occurring through the evaporation of magnesium to combine with oxygen at some distance from the surface to generate MgO which immediately condenses to smoke of perfect cubic crystals.

Some studies of the mechanism of oxidation and ignition of heated surfaces of magnesium and magnesium Dowmetal "C" were made. Slabs of the metal were cut from a cross section (3-7/16 in. square) of their respective pigs and machined to a thickness of 3/8 inch. To facilitate temperature measurements, a thermocouple well was drilled in the center of the block. The slabs were heated in a 6-inch-diameter stainless-steel pan on an open heating element whose temperature was regulated by a voltage control. The total heating time up to ignition averaged about thirty minutes. Changes in the samples and corresponding temperatures were noted.

The first series of tests, comprising several runs, was carried out on commercially pure (99.9%) magnesium slabs. Temperatures given below are averages of the several runs. The first change in appearance occurred at 550°C and consisted of the formation of a white powdery substance. By the time 575° was reached, the powder started to become gray; at 640° it had turned yellowish white. Just before the metal melted at 650° , the surface coating turned brownish black. Several attempts were made to collect samples of this black material for analysis; however, each attempt caused it to ignite and burn to a yellowish white ash. Analysis of the ash showed it to be 93% MgO . Although the yellow coloration would indicate the presence of nitride, chemical and x-ray spectrographic analysis failed to detect it. In the case of the x-ray procedure it is possible that proximity of the oxide bands to the nitride bands prevented their detection. From these results the various compounds formed on the metal surface as the temperature rose were judged to be suboxides. No accounts of the composition of these successive formations have been found in the literature. The temperatures given should not be taken as critical ones because the relationship involves time as well as temperatures. The changes will occur at lower temperatures if the heating time is prolonged.

It was observed during the tests that combustion, characterized by the familiar brilliant white flame, took place from a slag mixture of metal and oxide. When a new surface of molten magnesium is exposed, it is silvery bright and no burning takes place. Only after the intermediate oxidation processes occur, as described above, does the ignition start. The most vigorous fire is made by mixing the "catalytic" oxide into the underlying molten metal and making it all into a pasty mass. It is not evident how this mechanism fits into that of magnesium burning during the vaporization process described above unless a temperature rise induced through the oxidation reaction itself (Constable effect) was required to supply vaporized metal fuel in sufficient amounts. During the burning process a constant expansion took place and the fire mass crept over the edges of the pan and pushed up fungoid formations. Figure 2 shows the peculiar magnesium metal formation remaining from a fire which has been extinguished and the oxide-nitride leached out.

Similar ignition tests were conducted with slabs of the magnesium alloy Dowmetal "C" (Melting Point 575° ; for analysis see Ref. 13) in the same manner as for pure magnesium. When the temperature of the slab reached 430° a "weeping" was noticed at the oxide film. At 480° to 530° the surface nodules rapidly increased in number and by the time the melting point of 575° was attained the oxide was black and ignition started.

Gasoline ignition of magnesium was studied by heating magnesium (Dowmetal "C") slabs 3-7/16 inches square, varying in thickness from 1 inch to 1/16 inch and secured in a wire basket 4 inches over a 12 by 12 inch surface of burning gasoline. Chromel-alumel thermocouples were spaced 1 inch apart and peened into the samples to record the increase in temperature. The tests were conducted in a closed room to eliminate wind effects on the gasoline flame.



Fig. 2 - Cross section of magnesium metal formation from an extinguished fire

Preliminary tests using an iron slab indicated the hottest portion of the flame to be 4 inches above the fuel surface where a steady temperature of about 560°C prevailed. Figure 3 traces the heating rates of the various thicknesses of magnesium slabs and indicates the observed ignition temperatures of each. First of note is the increased length of time needed for heating and ignition of the heavier sections. These heavier sections appear to have a slightly lower ignition temperature but this is believed due only to the different oxidation characteristics of the slabs. With the thin slabs the temperature rises so rapidly the oxidation does not have time to proceed before the higher temperatures are reached. With the thick slabs the oxide formation keeps pace with the temperature rise, and as is very evident in the case of the 1-in.-thick piece, the oxidation itself provides the necessary "kick" in temperature to trigger the ignition.

It is theorized that actually the ignition temperature of magnesium is always the same and occurs at its boiling point of 1080°C . This high temperature is reached through auto-oxidation heating at minute local points not detected in observing the general temperature of the mass.

SMALL-SCALE MAGNESIUM FIRE EXTINGUISHING TESTS

Comparative Tests of TMB and Other Agents

Previous investigators seeking materials suitable for extinguishing magnesium fires have reported difficulties in setting up a standardized test procedure for making comparative evaluations of agents (1,2,3) and this research project was no exception. The approach of Greenstein and Richman (3) appeared to show the most promise. In their work they heated a confined mass of magnesium to a fixed temperature of 1000°C and then measured the amount of agent required to lower the temperature of the mass to its solidification point of 650°C . This made a convenient end point for calling the fire "out," an otherwise difficult point to determine by visual appearance. A cooling-time curve comparison was taken as a good relative evaluation of extinguishing ability.

Attempts to utilize the test procedures of Greenstein and Richman soon led to problems which were considered impractical of solution. Their conditions of test also showed a wide departure from the expected conditions of application of aircraft magnesium fire extinguishing agents in that they employed a large molten mass with a relatively small burning surface area.

The foundry sand molds recommended in their tests were difficult to use as container for molten magnesium because of their tendency to split or channel and allow access of air to the sides and bottom of the molten metal. The resulting irregular burning and oxidation rendered any temperature-vs-time measurements invalid. When iron containers the same size were tried, some new variations in the burning mechanism of the molten metal were demonstrated. Evidently the high ratio of mass of metal to exposed surface leads to the formation of channels up and down along the wall, promoting irregular oxidation and formatic

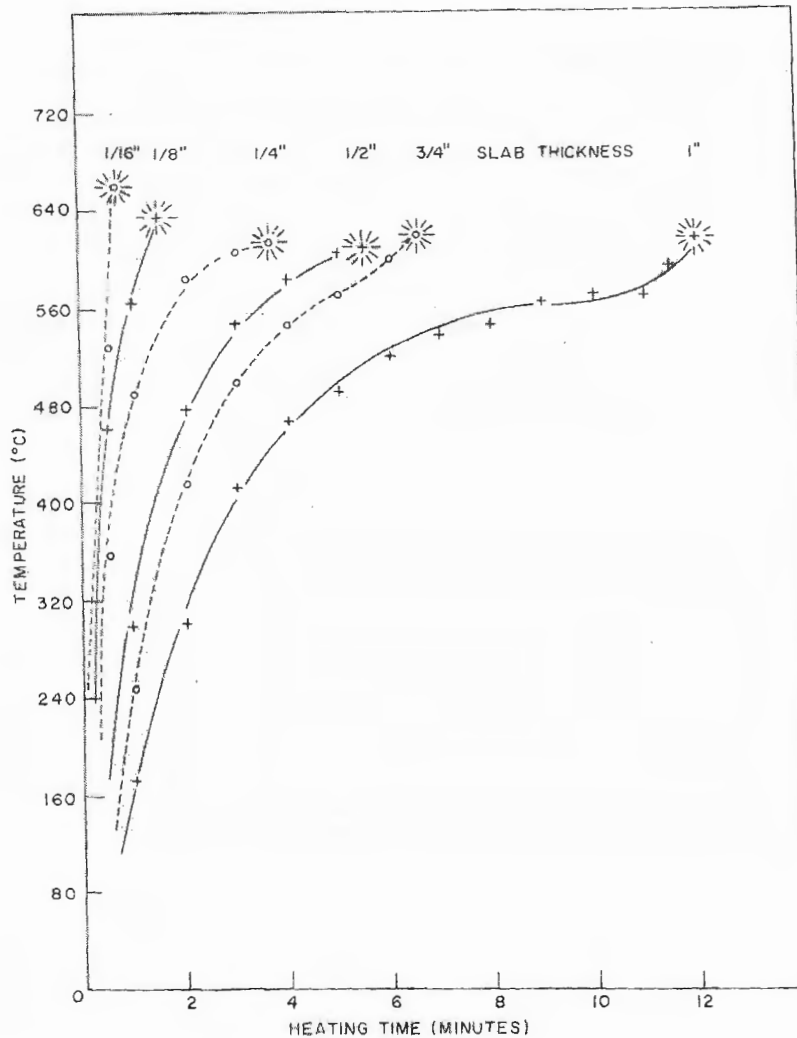


Fig. 3 - Heating and ignition of magnesium slabs suspended over a gasoline fire

masses of fungus - like oxide growths which further aid in allowing the metal to "creep" and expose itself to air. Again, it was very difficult to obtain concordant temperature-vs-time measurements from test to test.

Granting the fact that the cooling curves which should be obtainable with this type of test show the superiority of an extinguishing agent with the greatest heat capacity, the test conditions are only distantly comparable with the variables encountered in aircraft magnesium metal fire extinguishment and control. In the latter case, the ratio of molten metal mass to burning area is usually very low and the economy of providing an extinguishing agent capable of completely cooling the hot metal could be questioned in view of the large quantities of water and foam normally available.

In order to utilize the unique character of TMB as a B_2O_3 carrier, it was desired to to use a completely different type of extinguishing mechanism - that of applying an impervious coating to inert the metal surface. It is anticipated that the fires normally encountered in aircraft would involve "skin" metal sheet and light castings which have a relatively large surface area and are supported above the ground. There would probably be a minimum of conditions existing where in any appreciable amounts of molten magnesium in deep pools would occur.

Attempts at burning magnesium in a vertical position in a uniformly progressive manner failed because the ignited portions fell off, resulting in self-extinguishment of the fire. The small-scale fire which was finally adopted as the standard fire for test purposes was chosen because it was representative of actual fire conditions and could be duplicated with a reasonable degree of accuracy. A container made of 1/16-inch-thick stainless steel, 6 inches in diameter and 5/8 inch deep, served to hold the 400-gram charge used for each test. A chromel and an alumel lead were peened into the pan bottom 4 inches apart to serve as a thermocouple averaging the bottom temperature over a wide area (Fig. 4). The charge was first melted by passing an oxyacetylene torch over the surface, and then as ignition took place, the contents were stirred up until a homogeneous burning mass was obtained. From this point on there was no molten metal interface present. As an equilibrium temperature was reached at about 900°C, the content were leveled off to give as uniform a surface as possible and the fire was then taken as ready for the application of extinguishing agent.

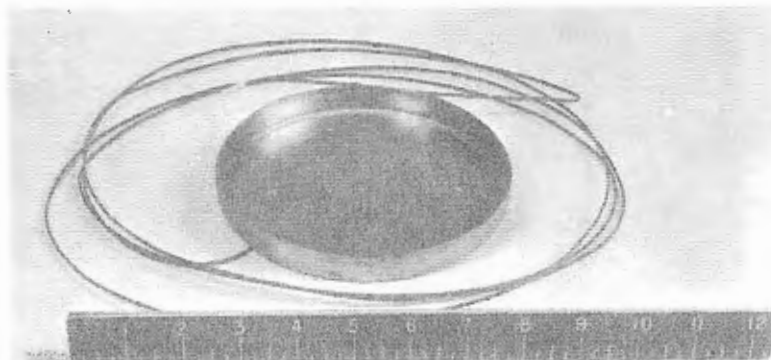


Fig. 4 - Small-scale fire test pan with thermocouple

The agents selected for comparison with TMB included the two new liquid agents resulting from recent Air Force development contracts together with two older commercial powder products. Specifically, they were:

TEG-Boric acid (Liquid)	88% by weight triethylene glycol
Ref. (2)	12% ortho boric acid
CB-DIDP (Liquid)	50% by weight chlorobromomethane
Ref. (3)	50% diisodecyl phthalate
Powder "A"	Free flowing sodium chloride composition
Powder "B"	Graphite and organic phosphate mixture
Air Foam	expansion 8, drainage time 4 minutes*
	expansion 4, drainage time 2 minutes

Liquid agents were applied to the burning magnesium from a pressurized extinguisher in the form of a gentle, low-velocity straight stream at the rate of 100 grams per minute. Pressures and orifice size were adjusted to compensate for the varying agent viscosities. Powder agents were poured on from a beaker at the same rate of

*These values for foam expansion and drainage time designate the characteristics of the foams used and were obtained in accordance with the methods given in NFPA Pamphlet No. 11, "Standards for Foam Fire Extinguishing Systems."

100 grams per minute. Applications continued until the thermocouple indicated a temperature of 600°C (50°C below solidification point).

In general the TEG-Boric acid liquid application was characterized by a considerable amount of hydrocarbon "secondary fire" and copious amounts of black, carbonaceous smoke. A residue of carbon and some boric oxide remained. The CB-DIDP application was also followed by a cloud of carbon smoke but with the addition of choking vapors originating from the decomposition of CB. A thin black residue was left on the magnesium. Powders "A" and "B" exhibited little or no vigorous reaction when spread over the fire. The application of TMB produced a large quantity of white smoke and also a small, green-colored secondary fire which was caused by the burning of methanol, methyl borate, and some of the TMB compound. The gray viscous material which remained on the metal boiled and frothed up into an expanded foamy tenacious coating, which hardened on cooling.

An analysis of the average cooling curves for the liquid agents (Fig. 5) shows that 2.0 minutes of application time (200 grams) of TEG-Boric acid were required to reduce the temperature to the 600-degree level, while 2.35 minutes (235 grams) of CB-DIDP and 3.35 minutes (335 grams) of TMB were needed to accomplish the same temperature reduction. The total heat absorbing capacity for CB-DIDP is 181 calories/gram and for TEG-Boric acid is 250 calories/gram. The total heat removed from the burning magnesium mass was 50,000 calories and 52,500 calories for TEG-Boric acid and CB-DIDP, respectively. Owing to the complex nature of its decomposition and vaporization, a comparable figure for TMB could not be determined. However, by assuming an average initial heat content of 46,500 calories and working backward, a heat absorbing capacity of 139 calories/gram is calculated.

Figure 6 shows the cooling curves for the two powder agents when the agents were applied until the temperature of the burning magnesium mass had been reduced to 600°C. The comparable cooling curve for TMB is also shown. Proprietary powder "A" required 5.7 minutes (570 gm calc.), proprietary powder "B" required 5.8 minutes (580 gm calc.), and TMB required 3.4 minutes (335 gm calc.) to accomplish an equivalent temperature reduction. The cooling ability of the powders appears higher than might be expected considering they possess no heat of vaporization properties; however, their heats of fusion probably contribute significantly to their heat-absorbing capabilities. Test conditions were ideal for the powder agents because it was possible to build up a deep layer of powder adequate to exclude oxygen from the horizontal fire surface and thus effect extinguishment.

Mechanical foam of 8 expansion and 4 minute drainage time was applied to a similar test fire and immediately the temperature rose from 915° to 990°C. During a second test, 4 expansion, 2.2 minute drainage time foam gave the same temperature increase. In both these applications the foam was added at such a rate that 100 grams of water were applied per minute. As the first foam contacted the burning area an instantaneous breakdown of the foam occurred. However, as more foam was added, it was possible to form what appeared to be an integral blanket. There was no violent reaction between the solution draining from the foam and the hot magnesium. The temperature continued to hold at a high level and later examination showed complete conversion of the metal to oxide.

TMB exhibits little foam-breaking tendencies and should not interfere with normal foam operations being conducted on surrounding hydrocarbon fuel fires.

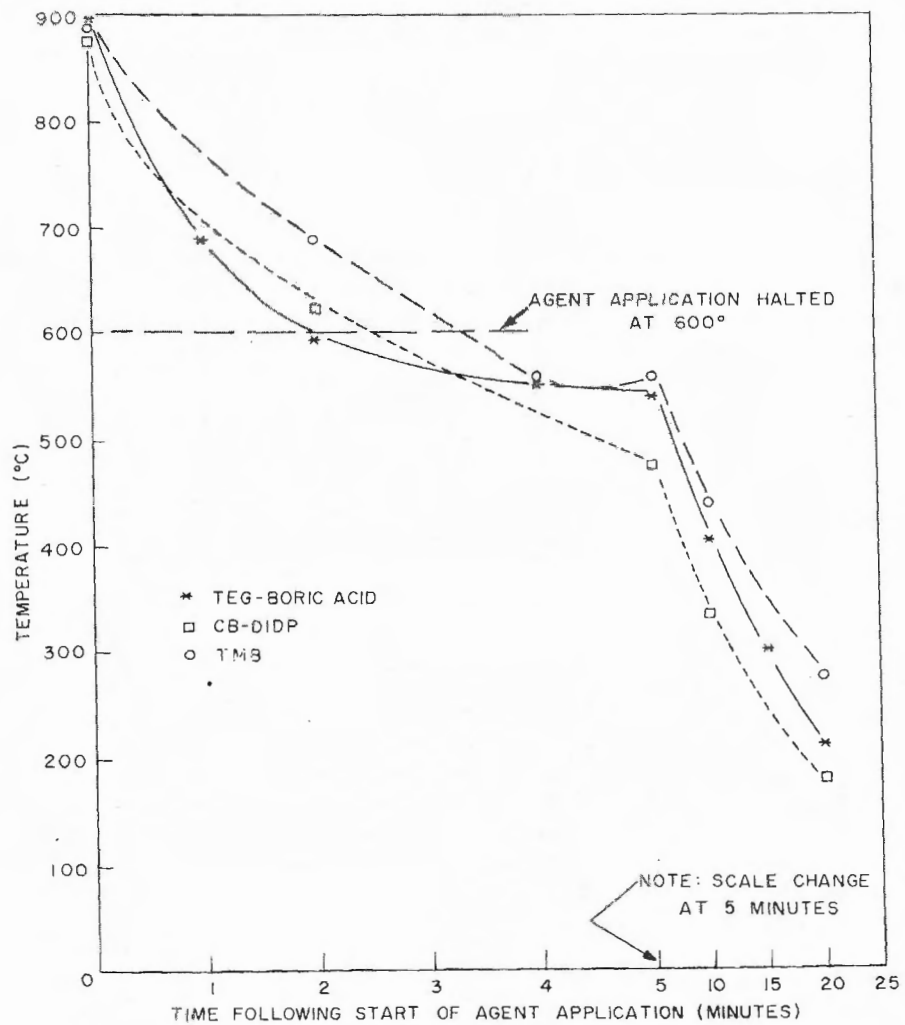


Fig. 5 - Averaged cooling curves for liquid agent application on small-scale fire test with Dowmetal "C"

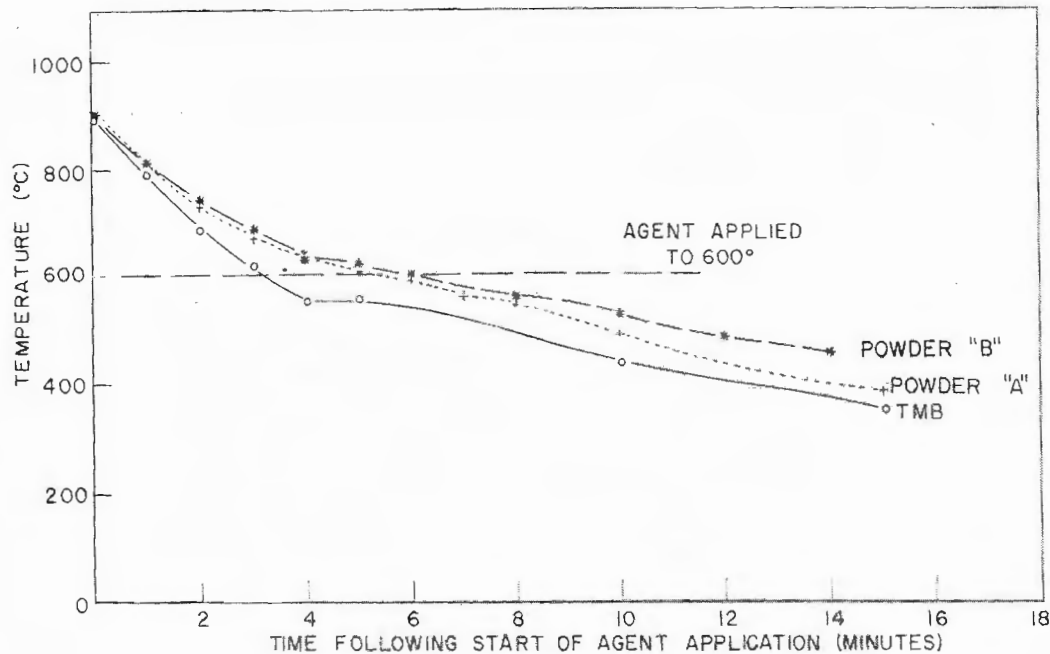


Fig. 6 - Cooling curves for powder agents and TMB application on small-scale fire test with Dowmetal "C"

Agent-Water Combination Cooling Tests

At this point in the research program it was realized that combustion or rapid oxidation of magnesium occurs in two ways. One mechanism is the burning through vaporization, evidenced by the brilliant flame and evolution of MgO smoke. This will initiate with the metal mass at a temperature slightly above or below the melting point depending on the rate of heating and the suboxide formation. Although the theoretical temperature of this flame is nearly 5000° (13), the underlying mass in these test fires usually remained 100° - 200° below the boiling point of 1100° . This type of combustion phenomenon takes place at the surface where the oxygen supply is plentiful.

The second type of burning takes place at a much reduced rate and without external visual evidence of flame or smoke. No exact temperature range measurements were taken but it is above the melting point and below $1100^{\circ}C$. It is characterized by a dull red color which is visible when the mass is not hidden under too thick a coating of oxide and the incident light is not too bright. Also, it is not a surface reaction but takes place simultaneously throughout the entire mass. Both types of burning will completely convert the metal to the oxide. These mechanisms can be compared to wood burning in the early stages with gases being evolved, and in the later stages burning directly as solid charcoal embers.

TMB and CB-DIDP were found to be very effective in knocking out the brilliant fire, however, if application was stopped at this point, the metal would continue to burn in the glow stage until consumed. During this period it would not constitute a particular hazard but would serve as an ignition point for aircraft fuel vapors. It was discovered that a straight stream of water could be applied at this stage without causing any reaction. This offered promise of a new technique in extinguishing the magnesium fire. The amount of agent required to cool the metal down below its solidification temperature is considerable, and the small volume available on an aircraft fire-fighting vehicle would limit extinguishing capability to small fires. However, if the metal fire could be inerted by means of an

agent and then cooled with the available water, it would greatly extend the efficiency of the agent. Furthermore, it is believed that the indicated cooling efficiencies found in this and other small test fires where conditions permitted the liquids to be retained until evaporated could not be obtained in field experiences, where agent run-off and misdirected streams will be prevalent.

The cooling rates which result from this combination technique when used on the small-scale fire were measured. The standard fire was kindled and the subject agent applied for one minute. It was observed that the white fire was knocked out within about 5 seconds by TMB and CB-DIDP application. After a delay of thirty seconds needed to manipulate the apparatus, water was applied as a straight stream at 100 grams per minute to effect further cooling. The data obtained are plotted in Fig. 7 for the three liquid agents. From the TEG-Boric acid curve it is seen that this material provided no protection against reaction with water and as a result the fire and temperature built back up to their original level. On the other hand both the TMB and CB-DIDP protected the magnesium surface to the extent that no reaction occurred even though the magnesium mass was at 800°C. Other experiments showed that a 30-second CB-DIDP application would provide sufficient protection to permit water addition with magnesium temperatures as high as 900°C. These also showed that if water was not used following the agent application the magnesium would cool without reignition to the white flame stage. This ability to protect the hot metal surface was most pronounced with CB-DIDP followed by TMB and then TEG-Boric acid which was effective to a much lesser extent. Greenstein and Richman (3) found this property to vary with the source and batch of CB used; however, this factor was not investigated in this work.

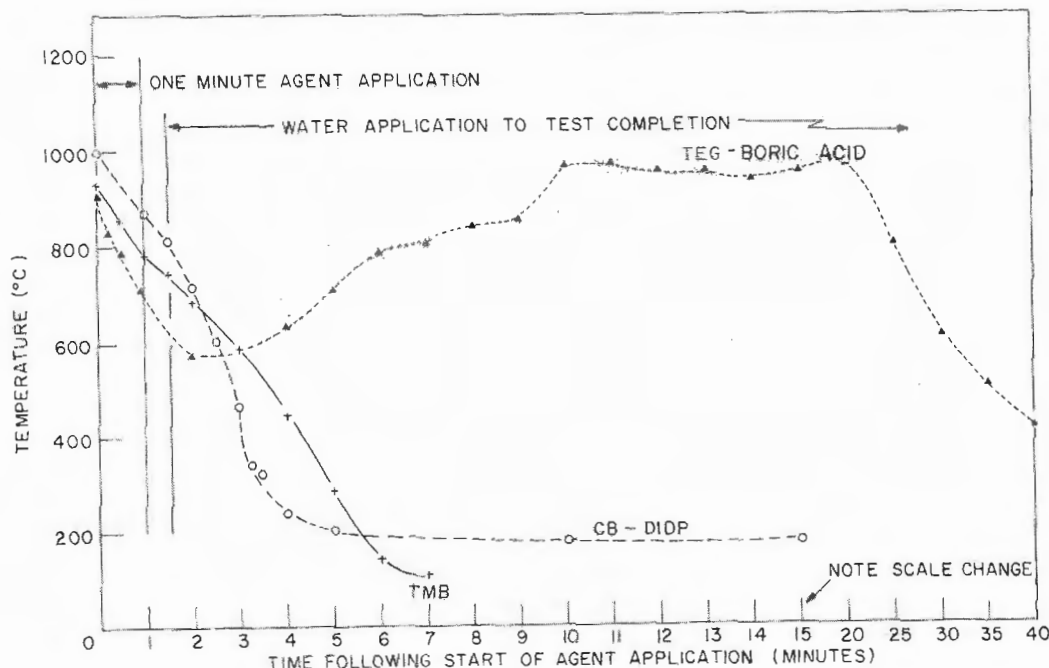


Fig. 7 - Cooling curves for liquid agents followed by water application on small-scale fire tests

It is believed that this dual technique of inerting the magnesium to enable the application of water with its high total heat capacity of 615 calories per gram offers real possibilities in combatting magnesium fires occurring in aircraft. From work done to date, the presence of magnesium vapor fires appears to be the critical factor in

determining whether or not water can be applied without a reaction occurring which will only intensify the fire. Much more field experience in fighting this type of fire is needed before the optimum procedures can be presented in more detail.

ADDITIONAL STUDIES OF THE PHYSICAL AND CHEMICAL CHARACTERISTICS OF TMB

The successful application of TMB liquid as a practical fire extinguishing agent for magnesium metal fires in crashed or burning aircraft depends to a large measure on its adaptability to field operations. Several of its present characteristics create potential problems in field use. These are:

- (1) Low viscosity index of the liquid
- (2) Comparatively low flash point
- (3) Solubility of gases
- (4) Hydrolysis of the liquid in the presence of water

Since TMB showed promising capability as a magnesium fire extinguishant, an experimental program was undertaken to determine the possibilities of changing or ameliorating some of the detrimental characteristics of the liquid.

Addition of Methanol to Improve the Viscosity Index

TMB's rapid increase in viscosity with lowering temperatures results in reduced flow rates and less effective nozzle patterns. Studies were made on the use of methanol as an additive to improve the viscosity index. Table 1 shows the effect of three additions of methanol on the viscosity of TMB at various temperatures.

TABLE 1
Viscosity of TMB with Methanol Added

Temp. (°C)	Viscosity (centistokes)			
	TMB 100%	TMB +1% Methanol	TMB +3% Methanol	TMB +5% Methanol
0	120.0	108.4	76.6	60.1
25	12.0	11.2	9.7	8.7
50	3.6	3.5	3.3	3.1

An undesirable side reaction took place when the methanol concentration reached 3% a formation of flocculent precipitate was observed to take place on standing. Small amounts of the precipitate could be driven back into solution by heating the liquid in a water bath. However, if the samples were placed in an ice chest and allowed to cool, precipitation reoccurred. As the methanol concentration was increased, the precipitate formed more rapidly, being instantaneous at a concentration of 10% methanol. A determination of the composition of the precipitate showed that it contained 99.35% boric acid (H_3BO_3) by weight. The loss of boric oxide content (due to its precipitation as boric acid) in the remaining TMB liquid after the addition of methanol was determined by titrating a sample of the clear supernatant liquid with standard base. A maximum decrease in boric oxide content was 10% which occurred when the methanol added was 40% to 50% by volume.

The optical transmission of these same samples was taken and the percent transmission decreased from 97 percent for 1% methanol to 3-4 percent when the liquid contained 40% to 60% by volume of methanol. The transmission then increased to 97 percent when concentrations of 70% methanol and above were reached causing all the precipitate to redissolve.

When the precipitate was first observed at the lower concentrations it was thought that the water content in the c.p. methanol was reacting with the TMB. To rule out this possibility, Eastman spectro-grade absolute methanol was used which in a Carl Fisher type determination of the water content analyzed 0.33 mg water/ml methanol, or 0.041 weight percent. There appeared to be no difference in the amount of precipitate formed between the two grades of methanol used during the tests.

Although the data in Table 1 show a reduction in viscosity on the addition of methanol, the viscosity index over the range of 0° to 25°C was not improved significantly. Because of its limited effect on viscosity, its precipitation reaction, and its flammability characteristics, methanol was judged an unsuitable additive for TMB for fire fighting uses.

The viscosity of TMB may be adjusted by varying the boric oxide content with methyl borate. Above approximately 60% boric oxide the viscosity of the TMB increases very rapidly.

Additives to Raise the Flash Point

As stated previously the flash point of TMB was found to be about 14°C and it was deemed desirable to raise this in order to promote safety in handling. Of the various halogenated hydrocarbons useful for inerting purposes, the first agent tried was chlorobromomethane, which when added in the amount of 10% by volume raised the flash point to 24.4°C. The flash point thus appeared to increase 1°C for each 1% addition of chlorobromomethane, within the range examined. Tetrachlorodifluoroethane ($\text{CCl}_3\text{CClF}_2$), which has a melting point of 40.6°C, was tried next. This raised the flash point slightly less than the same percentage addition of chlorobromomethane; the flash point was increased to 23.3°C when the volume of this agent added was 10%.

Monobromotrifluoromethane (Freon 13-B-1) was then bubbled through TMB and the flash point of the resulting solution was determined. It did not flash when the temperature was raised to 96°C, at which time the vapors began to burn on the outside of the cup. It was evident from these tests that, of the agents tried, this had the greatest influence on the flash point; however, it also had the disadvantage of high solubility in the liquid.

Solubility of Various Gases in TMB

Since liquid TMB will probably be used in an extinguisher utilizing gaseous expellents the solubilities of the possible gases such as air, nitrogen, carbon dioxide, and Freon 13-B-1 in TMB were determined at a temperature of 25°C at pressures of 50, 100, 150, and 200 psig. The apparatus used for these measurements consisted of two small, high-pressure bottles connected by a manifold to which a gage was attached for reading pressure changes. A 500-ml sample of TMB and an atmosphere of the gas under test were placed in one bottle, and the gas under pressure in the other bottle. After temperature equilibrium had been reached, the cross-over valve was opened and the bottles shaken until the gage indicated establishment of a constant pressure. The difference between the observed and theoretical pressures permitted calculation of the volume of gas dissolved. The results are summarized on the following page:

Gas Solubilities in TMB

Gas	Solubility (ml/L/1 psi)
Air	2.4
Nitrogen	2.7
Carbon dioxide	214.
Freon 13-B-1	271.

As will be brought out later, high gas solubility is detrimental when applying TMB because of flash volatilization on release from the extinguisher.

Studies of the Hydrolysis of TMB

The reaction of TMB and water presents a potential trouble source in the field use of the material. The hydrolysis creates a solid material, boric acid, which may clog small passages and interfere with extinguisher operation. This precipitating reaction also removes the effective ingredient, boric oxide, and will reduce the efficiency of the original liquid. Studies were initiated to investigate TMB's hydrolytic tendencies and to devise adequate protective procedures for the storage and handling of extinguishers.

A sample of TMB spread out on a glass slide and exposed to an atmosphere of 50% RH will completely "skin over" within 15 minutes. A 250-ml sample of liquid was exposed in a 400-ml beaker to a relative humidity of 50%. After an exposure of two days there resulted a 17% decrease in volume and a refractive index increase from 1.3977 to 1.4036 at 25°, which increased further to 1.4039 after a total of 3 days exposure. Due to the loss of methanol, the boric oxide content of the sample also showed an increase from 58.7 to 62.1% by weight; the viscosity increased from 12 to 202 centistokes after two days exposure and to 254 centistokes after a total of three days exposure. While uncovered, both methanol and TMB are liberated, the latter building up a solid white precipitate of boric acid around the mouth of the beaker as it hydrolyzes from the vapor stage. The remainder of the TMB, not hydrolyzed on the mouth of the container, forms a white, shiny, slick, glaze coating on the glass and metal surfaces. The loss of volatile components results in the formation of a light skin or membrane across the surface of the liquid after it has been exposed for a period of time, which appears to hinder any further escape of the volatile components. The liquid remaining in the beaker becomes turbid, and a flocculent precipitate settles out if the sample is allowed to remain exposed to the humid air. The tight membrane gradually changes to a hard white crust.

Saturated air was aspirated through a 250-ml sample of TMB that was contained in a conical-shaped Milligan-type gas washer. The air was metered through the sample at a rate of 0.4 cubic feet per minute, and refractive index readings were taken at intervals during this hydrolysis run. The results appear in the tabulation on the following page.

The quantity of the sample was reduced to 190 ml which is a volume decrease of 24%. The sample contained a flocculent suspension which gave a turbid appearance. A determination of the physical characteristics of the sample revealed an optical transmission of 75%, and a viscosity of 876 centistokes at 25°C. The boric oxide content was 64.04% by weight, which represents a gain of 9.1% boric oxide per unit volume over the original sample.

Effect of Hydrolysis on Refractive Index

Sat. Air (cu ft)	Refractive Index at 25°C
0	1.3977
25	1.4019
43	1.4042
50	1.4048
60	1.4050
65	1.4059

It was desired to devise an adequate test procedure to detect the occurrence of hydrolysis that might have taken place in the field due to improper storage. Possible methods of measuring the degree of hydrolysis were by refractive index, infrared, and light transmission techniques.

The two hydrolytic products of TMB affect the resulting refractive index in opposite directions, with the boric acid tending to increase it and the methanol to decrease it. A calibration was made by adding water in definite amounts to TMB and then measuring the refractive index of the clear supernatant liquid after the precipitate had settled. A plot of the observed refractive index and B_2O_3 content with respect to the corresponding water content is given in Fig. 8. From these curves and a measurement of the refractive index of a TMB sample, one may determine the degree of hydrolysis, if any, which has occurred and how much B_2O_3 has been lost in the form of precipitate. The ability of TMB to extinguish fires with respect to its B_2O_3 content has not been studied; critical B_2O_3 data in this connection are not available. With careful heating, 20% H_3BO_3 could be dissolved, increasing the B_2O_3 content by about 16%; however, this is not feasible because of the higher viscosity which results.

In order to investigate the application of infrared analysis, another series of TMB samples was hydrolyzed and infrared spectra recorded. The determination of H_3BO_3 and methanol is dependent upon being able to measure the transmission at two separate wavelengths, each transmission being characteristic of one of these compounds. This was found to be impossible in the case of TMB; the only usable wavelength is at 2.9 microns but here the B-OH and C-OH bands are both absorbing and hence mutually interfering. Therefore, this method was judged as unsatisfactory for this purpose.

The third method investigated for determining degree of hydrolysis in TMB was a light-transmission technique. But because the H_3BO_3 precipitates out over a period of time leaving a clear liquid above, this procedure is also unsatisfactory. Thus, the refractive index determination is the most suitable method for detecting the occurrence of hydrolysis in TMB.

A check on the vulnerability of TMB to water vapor was obtained during the investigation. In the process of evaluating extinguisher operation it was necessary to make many flow-rate tests using different nozzle designs and charging pressures. Due to material shortage, TMB underwent as many as five charge-discharge cycles, each time being sprayed into the humid summer atmosphere of Washington with a minimum relative humidity of 50%. Careful analysis of the material failed to detect any evidence of hydrolysis through the handling. Therefore, it was concluded that TMB stored in a reasonably tight container would be in no danger of hydrolysis through atmospheric water vapor.

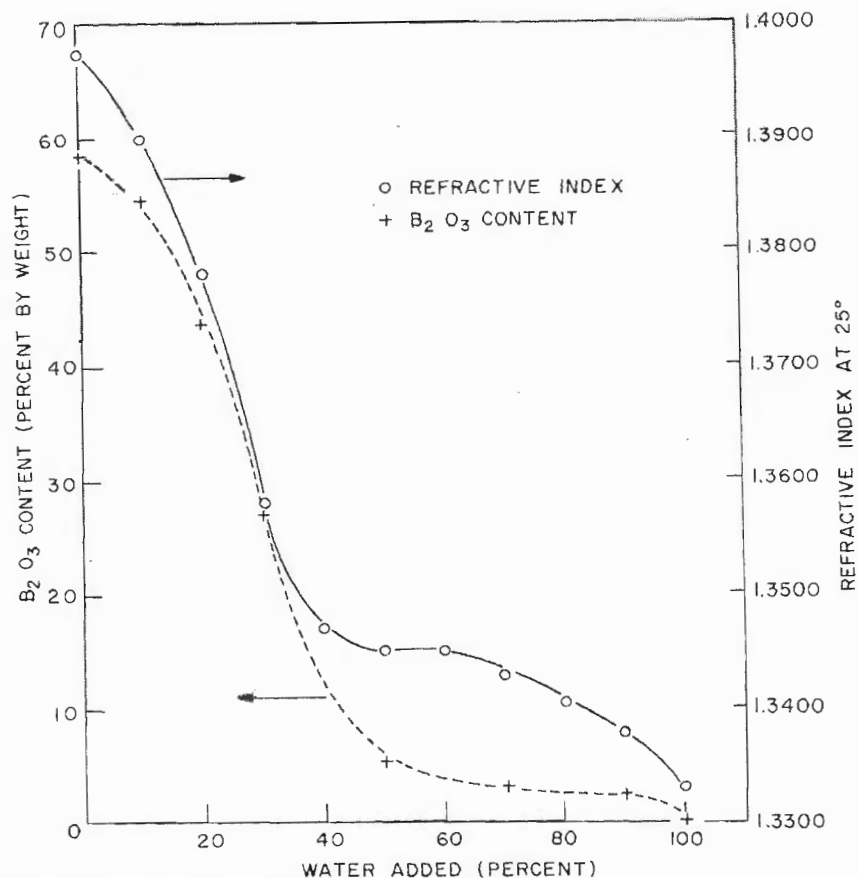


Fig. 8 - Variation in B_2O_3 content and refractive index of TMB on addition of water

Materials of Construction

A limited study was made of the corrosive nature of TMB toward some common metals used in extinguisher construction. Specimens of aluminum 5052, aluminum 1100, yellow brass, copper, stainless steel, and steel were made up in 1/16-inch-thick strips 3 in. long and 1/2 in. wide and immersed to three-quarters of their length in TMB contained in a lightly stoppered bottle. They remained at room temperature for four months, at the end of which time no difference in weight or appearance was observed. From these results it was concluded that TMB could be considered noncorrosive toward these metals.

It was noted that TMB adversely affected neoprene and some other rubbers. Accordingly, test specimens of several elastomers—smoked sheet rubber, GNA, Paracil AJ, Neoprene WRT, GR-I, and OR-25—were prepared and exposed to TMB liquid and vapor for a period of seven days. At the conclusion of the exposure the samples were examined and checked for tensile strength and percent elongation. Only the GR-I formulation was found to be essentially unaffected. Continued GR-I exposure of 3 months has shown no change and therefore its use is recommended for TMB service.

FULL-SCALE MAGNESIUM FIRE TESTS

Fire Tests Using Castings

Magnesium castings, in the form of quartered sections of aircraft wheels, were used in the early full-scale fire-test trials in an attempt to determine the comparative extinguishing efficiencies of the liquids used in the small-scale fires. Considerable variation existed, however, in the ignition and rate of burning and for this reason it was found impossible to effect a sufficient degree of reproducibility among fire tests using castings for a quantitative evaluation of candidate extinguishing agents.

Visual observations of extinguishing characteristics of these agents could be made, however, but they did not indicate any clearly superlative individual performances. All three liquid agents when applied to separate burning castings at approximately equivalent rates seemed to do equally well. Of the three agents, TEG-Boric acid solution resulted in the most persistent secondary fire; the CB-DIDP liquid caused the most disagreeable odor. Of the three, TMB alone developed a protective surface coating which prevented rekindling of "hot spots" in the magnesium mass.

Aside from these generalizations, this testing phase was influential in resolving the design of an ultimately acceptable liquid-agent extinguisher as being of the stored-air-pressure type. Among the other important findings of the casting-type fire evaluation were the desirability of a dual stream nozzle, the need for a controllable discharge valve to economize on agent use, and the necessity for maintaining simplicity of general extinguisher design to facilitate cleaning and recharging operations.

Fire Tests Using Sheet Forms

A chief difficulty in fire tests relating to solid combustibles, more so than with flammable liquids, lies in the difficulty in duplicating the fire situation. This is particularly true of the larger scale tests which necessarily must be conducted as field experimentation. At best, only a general degree of reproducibility can be achieved by reducing all possible variables to a minimum.

To facilitate a comparison of the available magnesium fire extinguishing liquids under consideration, sheets of various gages and shapes were put through initial tests. Thin sheeting, which burned readily at low wind velocities, was finally adopted for use because difficulties were encountered in igniting and maintaining uniform combustion in stock thicker than 1/16 inch.

The chosen geometry of sheet form arrangement, whose use resulted in duplicative fire tests and results, was constructed of seven 1/32-inch-thick FS-1 alloy sheets bolted into two separate assemblies (Fig. 9). The top vertical assembly consisted of five sheets 1 foot wide by 1-1/2 feet high bolted together at five points with 2-inch spacers between each sheet. The bottom horizontal assembly was made of two like sheets bolted together with the bolts extending 2 inches through the bottom to serve as legs. For the fire test the sheet assemblies were arranged as shown in Fig 9.

A propane gas torch of standard size and under a constant pressure of 30 psig was used in preheating the entire assembly for one minute and then in igniting each vertical section in rapid succession at approximately 1/3 of the distance up its edge. A preburn period of an additional 30 seconds was then followed by application of sufficient agent to extinguish all the burning magnesium completely. Each of the liquid agents used in the comparative studies was applied in a straight stream at average rates of 250 grams per second, from a 2-1/2-gallon extinguisher under the required stored air pressure. All tests were conducted with wind velocities of approximately 300 feet per minute to aid in maintaining a reproducible fire.

Figure 9 depicts the overall assembly appearance during the general preheating period, Fig. 10 the igniting technique, and Fig. 11 the appearance during preburn period. Figure 12 shows the similarity in appearance of three specimens following duplicate tests using the same liquid agent.

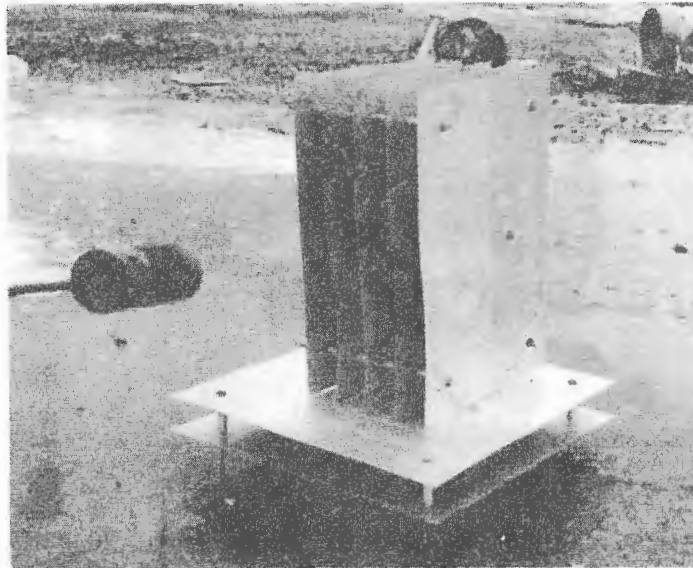


Fig. 9 - Preheating of magnesium sheet in the standard sheet form fire tests

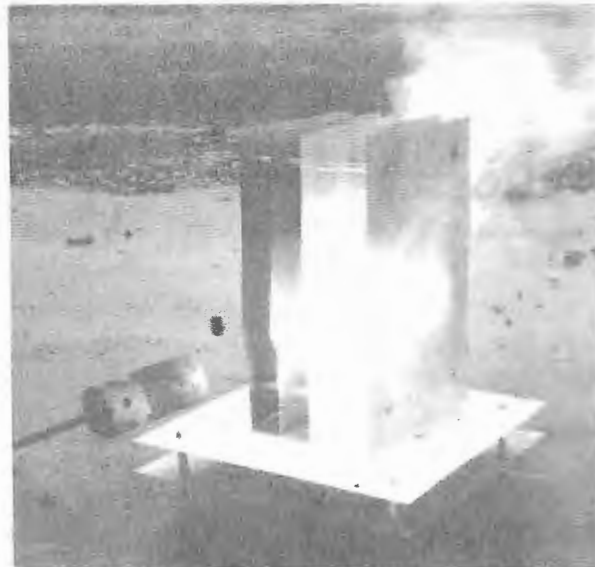


Fig. 10 - Ignition of magnesium sheet

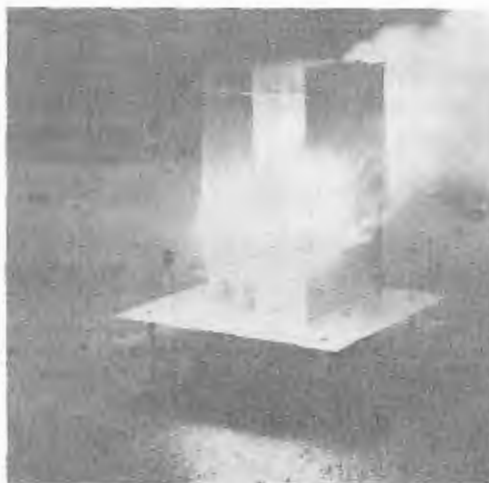


Fig. 11 - Preburn period of sheet

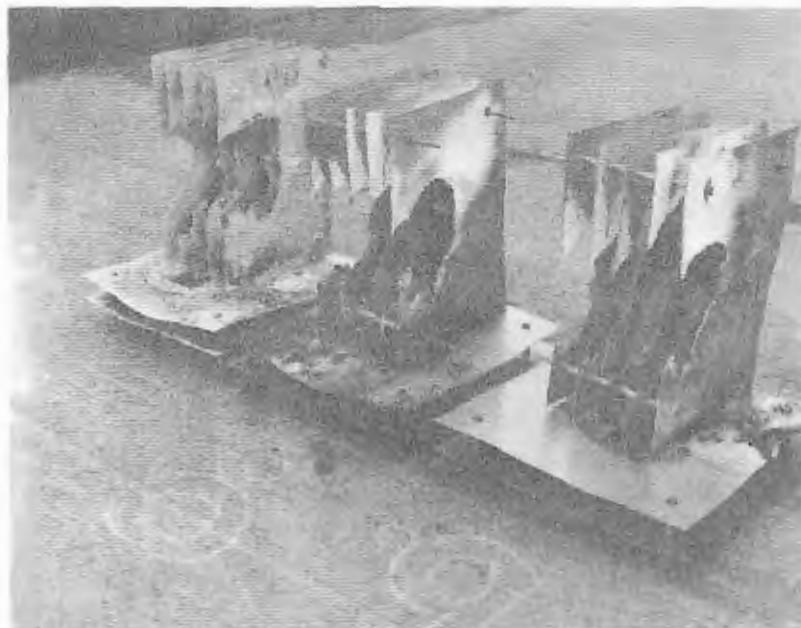


Fig. 12 - Extinguished standard magnesium sheets

Results of Sheet-Form Fire Tests

Using the newly developed sheet-form fire test, a series of duplicate fire extinguish runs was conducted utilizing the three liquid agents. Weight checks indicated about 200 grams of metal were consumed out of 2300 grams in each test. Table 2 summarizes the results and shows the close degree of duplication that was obtained with this procedure. Also included are the results of two single extinguishments, one with plain water and the other with a 50-50 by weight mixture of CB and TMB.

TABLE 2
Amounts of Liquid Agents Required to Extinguish Magnesium
Alloy Sheet-Form Fires

Agent	Amount of Agent Required - Grams			
	Test I	Test II	Test III	Average
TEG-Boric Acid	2255	1895	2549	2233
CB-DIDP	1569	1552	1305	1475
TMB	2469	2630	2310	2470
CB-TMB	1427			
Water	4815			

Analysis of this table reveals that CB-DIDP resulted in the fastest extinguishment, thereby using the least material, and is of the same order of efficiency as the CB-TMB solution. TEG-Boric acid and TMB were of the same general performance, but a considerable amount of plain water was needed to effect extinguishment.

DISCUSSION AND RECOMMENDATIONS

In the early stages on the problem of extinguishing magnesium fires the objective of complete extinguishment by the use of a single agent such as trimethoxyboroxine was considered to be most important. As the fire extinguishing tests of the various candidate materials progressed, the wisdom of this course became doubtful, because quantitative relationships could be obtained only with the sheet-form test fires. Use of field-scale casting-type fires, thus increasing the mass of metal, required inordinate quantities of agent to accomplish satisfactory extinguishment and cooling to a safe temperature below the flash point of gasoline.

When the operating variables are considered in attacking a fire in the magnesium components of an aircraft using conventional crash fire-fighting equipment, the existing obstacle which prevents the employment of water or foam (which are available in plentiful amounts with such equipment) is the reactivity of magnesium with water at the ignition temperature of the metal. If water could be brought into contact with the hot magnesium without reacting, its high heat of vaporization could be utilized and extinguishment and cooling would ensue with an economy and facility not possible with any other material.

Based on the small-scale pan fire tests, this study shows that the formation of a surface "skin" of glassy boric oxide, which results when TMB decomposes on burning magnesium, permits the cooling of residual metal by air or water without further generation of heat in the mass. The agent CB-DIDP accomplishes the same inerting action by a thin soot-like deposit on the surface.

A careful consideration of the results of the fire extinguishing tests led to the conclusion that for the metal fire systems which were devised (with a serious effort throughout to simulate conditions encountered in actual field situations) effective control and extinguishment of burning metal in a horizontal plane is achieved by all the powders and liquids tested. Furthermore, where liquids alone were tested against fires possessing horizontal, vertical, and depth dimensions, the CB-DIDP mixture provides the most rapid

and efficient extinguishment with TEG-Boric acid liquid showing roughly equivalent efficiency to TMB. The brief "flare-up" of TMB liquid applied to a fire is followed by a very minor secondary fire of short duration. Among the liquids tested, the CB-DIDP mixture showed little "flare-up" and little secondary fire, and TEG-Boric acid gave a moderate flare-up and a secondary fire of long duration. The mixture of CB-TMB shows extinguishing efficiencies in the same order of magnitude as CB-DIDP and in addition provides the beneficial qualities of TMB liquid alone. However, certain other factors exist in this picture which require consideration.

Extinguishers which expel powders are used best against fires which are within reach of their short range and low velocity and against horizontal surfaces which will permit the accumulation of an effective depth of the powder. They cannot easily be used against fires deep inside metal casings such as may be encountered when combatting fires inside turbo jet engines. The use of liquid agents, which are capable of greater projection distances from a suitable nozzle, is of definite utility in fighting aircraft fires and for this reason the powdered agents were dropped from further consideration.

The problem of toxicity of various materials is of prime importance in Naval fire fighting operations. The CB-DIDP liquid contains 50% chlorobromomethane which is definitely toxic when used as a fire extinguishant. Tests at the Underwriters Laboratories have shown it to be similar in its physiological action to carbon tetrachloride and in the same category when evaluated as to its comparative health hazards (14). Toxic risks of this magnitude are considered too serious for exposure of Naval fire fighting personnel when weighing the advantages gained. Materials of this toxicity can be justified only when their properties are unique and nothing else can be substituted. Such is not the case here.

One of the important factors in judging the utility of candidate materials for use as fire fighting agents is their reaction to temperature changes encountered in field usage. The TEG-Boric acid liquid shows an inordinate change of viscosity with temperature (Fig. 13). It is entirely probable that temperatures from 32° to 120°F will exist where these extinguishants will be stored and used, and the TEG-Boric acid liquid changes from a viscous, thick, syrupy material to a watery fluid in this temperature range. An additional drawback to the use of the TEG-Boric acid formulation is the magnitude and duration of the secondary fire which is generated by the burning triethylene glycol.

It is appropriate that some consideration should be given to the question of toxicity of the TMB liquid. Because of its rapid hydrolysis in contact with water, the parent compound could very well be considered a mixture of methyl alcohol and boric acid, both of which have well-known physiological effects, the alcohol being a serious toxicant when ingested and the acid being capable of absorption in areas of denuded skin. These conditions are seldom met with in crash fire extinguishment procedures.

The decomposition of TMB liquid when applied to burning magnesium can result in numerous pyrolysis products. Considering these possibilities, the resulting products in the atmosphere may be: trimethyl borate vapor, methyl alcohol vapor, water vapor, carbon monoxide, carbon dioxide, and perhaps finely divided elemental boron. To the extent and for the exposure time which could be expected in the atmosphere surrounding aircraft magnesium fire extinguishment using TMB, these compounds should have no serious toxic effects with complicated sequelae. No extended physiological studies have been conducted at this Laboratory to verify the safety of exposure to the decomposition products of TMB in fire extinguishment systems. A study on the low intrinsic toxicity of trimethyl borate has been reported (15) but lung ingestion was not included in the test conditions.

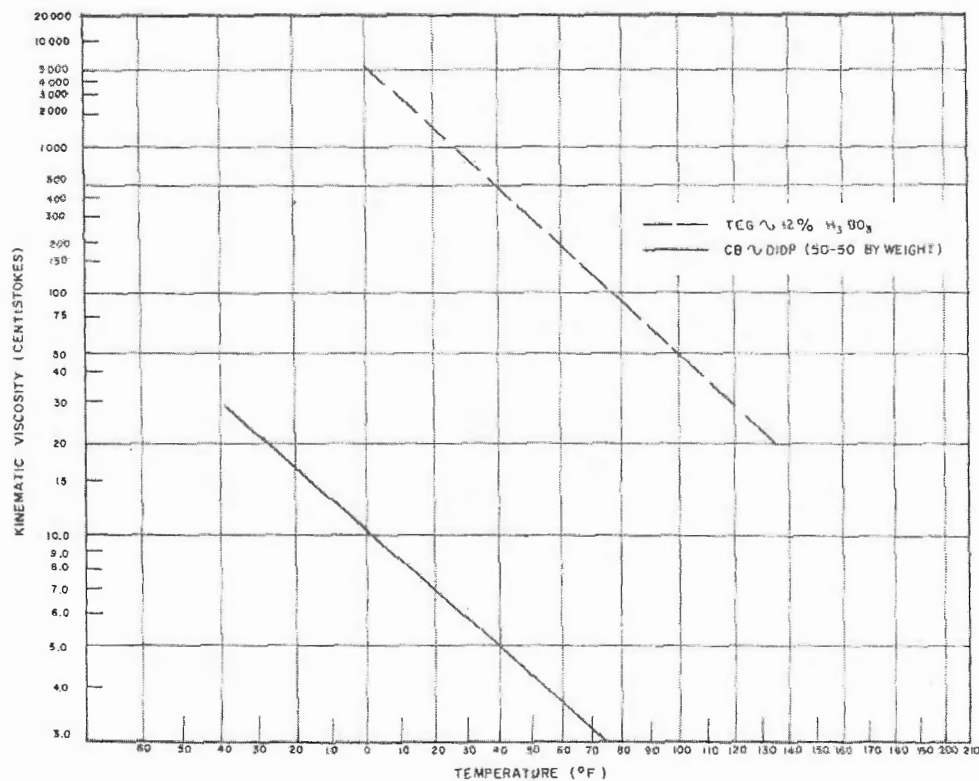


Fig. 13 - Viscosity temperature curves for TEG + 12% H_3BO_3 and 50% CB - 50% DIDP mixtures

The present cost of TMB is in the neighborhood of \$1.00 per pound or \$10.00 per gallon. This is relatively high in comparison to the other agents evaluated in this study. CB-DIDP is estimated at \$0.41 per pound or \$4.45 per gallon; TEG-Boric acid \$0.36 per pound or \$3.40 per gallon; Powder "A" \$0.25 per pound; and Powder "B" \$0.30 per pound.

After a careful and detailed weighing of the results of the foregoing investigations into the many aspects of extinguishing magnesium fires in Naval aircraft, it was concluded that TMB had more to offer than any of the other agents presently known. For this reason it has been recommended to the Bureau of Aeronautics for use on crash, fire, and rescue trucks in the form of portable 2-1/2-gallon extinguishers. In order to expedite the procurement of these extinguishers, a prototype model was developed and assembled by this Laboratory. This work together with a description of the unit is covered in Appendix A of this report. The specifications developed for the procurement of the TMB material is given as Appendix B.

The work done on improving the viscosity index and lowering the flash point has not revealed any suitable means for accomplishing these objectives, and the material is to be used without modifiers. The gas solubility results indicate air or nitrogen to be acceptable expelling gases for TMB while CO_2 and Freon 13-B-1 are not to be used because of their high solubility in the liquid. Hydrolysis studies showed that water vapor does not present any problem in the handling of TMB; however, liquid water should not be allowed to come in contact with TMB which is to be used in charging fire extinguishers. The occurrence and/or degree of hydrolysis may be determined from the refractive index of the supernatant liquid.

It is the intent of this laboratory to continue investigations on using the water-agent combination technique in extinguishing magnesium fires with the aim of improving their efficiency. A close surveillance will be kept on the TMB extinguishing units now going into the field to determine if improvements or modifications can be made. In addition research efforts will be continued to find even better agents.

ACKNOWLEDGMENTS

The authors wish to thank W. E. Franks and W. J. Quinlan of the Engineering Research Branch, who aided in many of the phases of the investigations reported herein.

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* * *

APPENDIX A

The Development of a Portable Extinguisher for Use with Trimethoxyboroxine

The objective of this phase of the project was to develop a prototype portable extinguisher and present recommendations to the Bureau of Aeronautics as to its manufacture and use in the aircraft fire fighting program.

GENERAL FACTORS INFLUENCING THE EXTINGUISHER DESIGN

For the unit to be functional as a portable item of fire fighting equipment, a 2-1/2-gallon extinguisher was considered to be the maximum size. From the preliminary magnesium fire fighting experience it was found that a dual-stream type of nozzle, giving either a spray or straight stream liquid pattern, was desirable. In addition, the total discharge time should be a period of from about 40 to 60 seconds at moderate (70°F) temperatures. Although several types of portable extinguishers for use with liquids are commercially available, they were not completely satisfactory to cope with the unusual properties of TMB. The special problems involved the high solubility of some gases in TMB, its low viscosity index, its attack on the common elastomers used for gaskets, hose, and seals, and its deposition of solid boric acid crystals when in contact with water. Other practical considerations involved the method of recharging, which is especially important in outlying bases, and the ease of dismantling for cleaning and inspection.

EVALUATION OF TWO COMMERCIALY AVAILABLE EXTINGUISHERS

The unit first tested was a stored-pressure type made by the American-LaFrance Corp. and identified as the Type D-2 extinguisher. It is a standard Air Force crash vehicle extinguisher for chlorobromomethane under an initial storage pressure of 150-175 psig. The features of interest were: a squeeze-type shut-off valve combined with the carrying handle, which could be used to regulate the liquid flow rate; a gage to indicate air pressure over the liquid; and a dual-stream nozzle on the discharge hose. The undesirable features which finally led to the abandonment of this extinguisher were: the permanently attached overfill preventer tube, the small neck opening which obstructed cleaning, the difficulties in disassembling and cleaning the discharge valve assembly, and the limited two-gallon capacity.

Consideration was given to the use of the 30-pound dry-chemical cartridge-type extinguisher for a TMB unit. It has a large neck opening for easy cleaning and the configuration would fit into the back-pack carrying harness developed for the foam-compatible dry chemical extinguisher. The cartridge system would provide a common recharging system with the compatible dry chemical extinguisher and would eliminate the need for a pressure gage with its vulnerability to plugging by boric acid deposits.

Fire tests with this extinguisher showed a markedly reduced efficiency and a tendency for the TMB to flash and burn in the air above the magnesium fire. This was traced to

the high solubility of the CO_2 gas being used as the propelling agent. The sudden release of pressure as the stream left the nozzle resulted in a rapid vaporization of gas which atomized the TMB into a mist, an ideal form for generation of flammable vapors. Moreover, much of the TMB was being lost by evaporation and misdirection. To prevent this action, it would be necessary to use special cartridges containing air or nitrogen, rather than carbon dioxide, thus introducing an additional supply problem.

The pressurizing problem and the weight disadvantage (twice the overall weight of a stored-pressure unit) were the deciding factors in finally abandoning the cartridge-type development in favor of a stored-pressure extinguisher.

DEVELOPMENT AND EVALUATION OF A PROTOTYPE STORED-PRESSURE EXTINGUISHER

The 2-1/2-gallon stainless-steel stored-pressure extinguisher manufactured by the Elkhart Brass Co. for use with water was chosen as the basic unit for developing the prototype TMB extinguisher. It has a large neck opening, a removable overfill preventer tube, and an easily dismantled valve assembly all of which simplify the cleaning and recharging operations.

The standard discharge nozzle was replaced with the dual-stream nozzle from the D-2 extinguisher, the "O" rings were replaced with others made from GR-I material, and the pressurizing and gage connections were fitted into a common connection on the valve assembly. After making these modifications (Fig A1), many discharge flow rate and pattern tests were conducted using air at various charging pressures and temperatures in order to establish the operating limitations. Low-temperature work indicated 32° F to be the minimum point where acceptable stream range and patterns could be obtained. At this point the TMB viscosity is 120 cs. Discharge flow rates were measured at temperatures of 72° and 32° F with varied charging pressures (Figs. A2 and A3). From these data an initial air pressure of 125 psi was selected as being the minimum acceptable for proper operation. Figure A4 shows the nozzle ground patterns of the TMB streams at the minimum temperature and pressure and also at 72° F with the minimum recommended pressure.

During the charging and discharging operations throughout the test period, a close observation was maintained on the formation of boric acid and its possible effect on extinguisher operation. Very little difficulty was encountered from this source. The small drilled passages in the head assembly could be easily opened by rodding, and the valve itself could be readily disassembled. Only the pressure gage presented a problem as no method could be found to seal off the Bourdon tube from liquid or to clean the interior of the tube. It was concluded that the best solution was to furnish a new replacement gage for each recharging. As an added precautionary measure to prevent any moisture from entering the extinguisher, it is recommended that the pressurizing air be passed through a drying cartridge when recharging the unit. Such a drier will be supplied with each extinguisher, and attached to the drier will be a moisture indicating "eye" to show the condition of the desiccant.

The Ansul Chemical Co. of Marinette, Wisconsin, has been awarded the contract for the initial production run of extinguishers based on the prototype stored-pressure extinguisher. Two such units will be mounted on the new MB-5 vehicle as part of its original equipment. For rapid identification in the field during fire fighting operations each extinguisher will be marked with a band of fluorescent "blaze orange" paint.

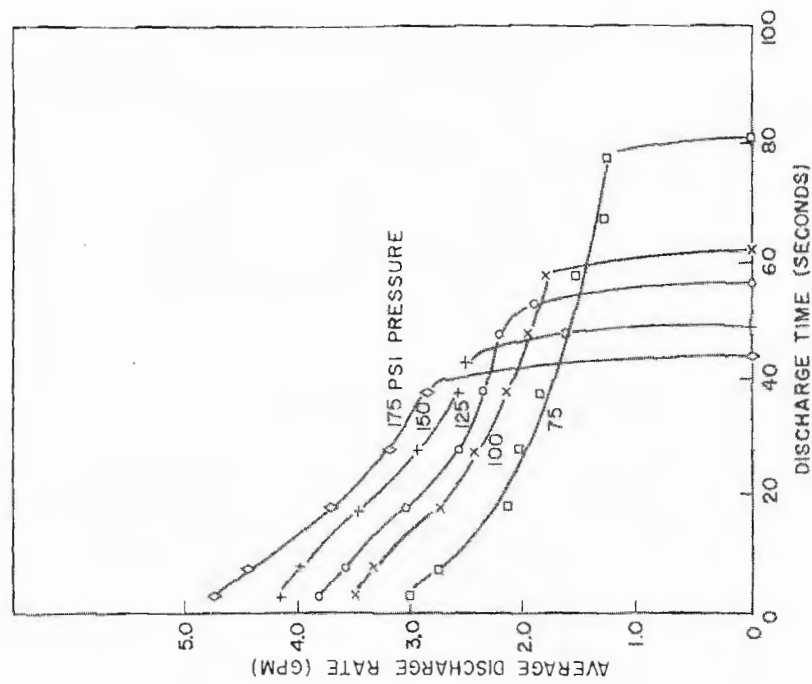


Fig. A2 - TMB discharge rate for varied initial charging pressures with prototype extinguisher - 72°F

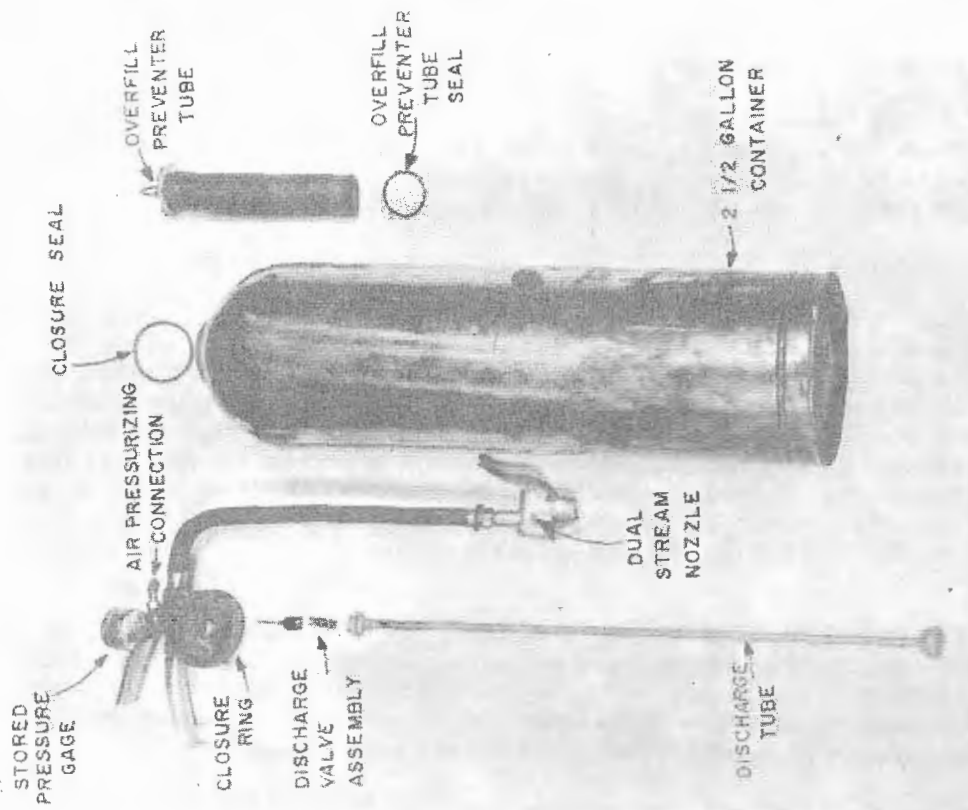


Fig. A1 - Exploded view of final prototype 2-1/2-gallon extinguisher for TMB

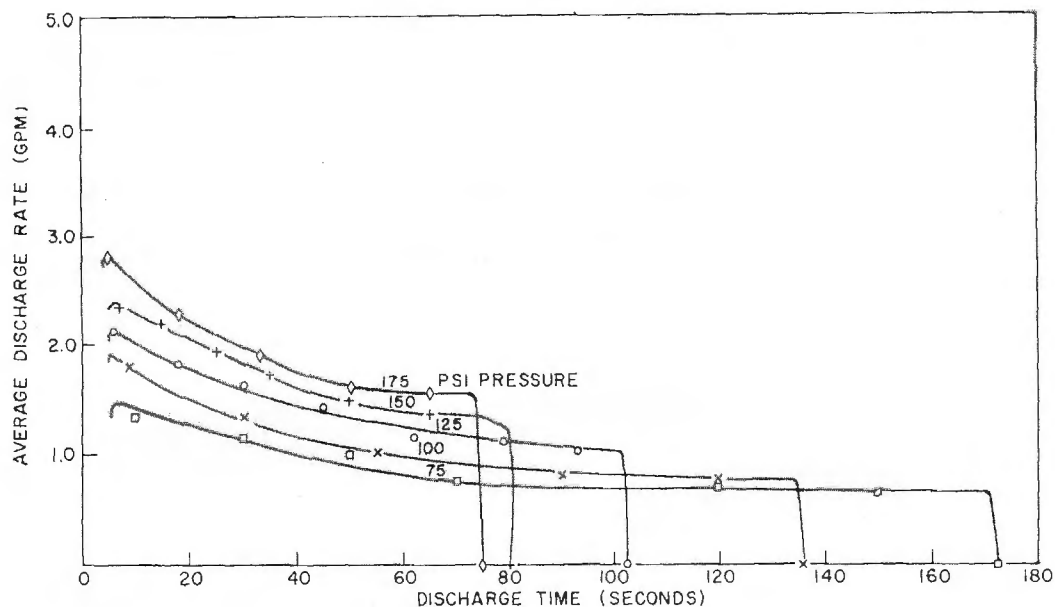


Fig. A3 - TMB discharge rate for varied initial charging pressures with prototype extinguisher - 32° F

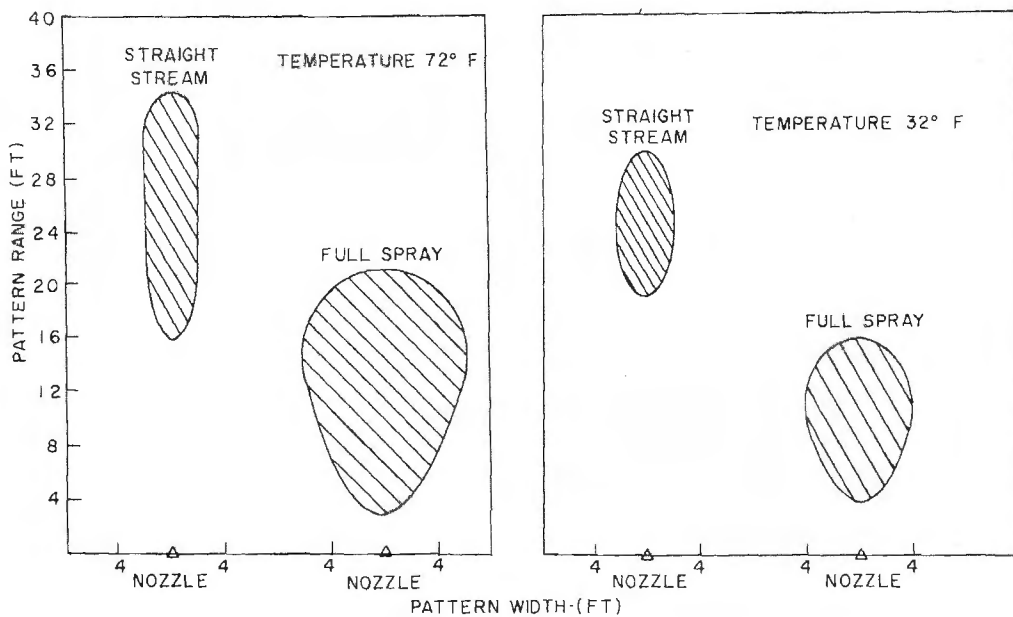


Fig. A4 - Ground discharge patterns using TMB in prototype extinguisher 125-psi initial pressure 72° and 32° F

APPENDIX B

MILITARY SPECIFICATION

Fire Extinguishing Agent, Liquid, Boron
Type, for Metal Fires

1. SCOPE

1.1 This specification establishes the detailed requirements for a nonaqueous chemical liquid fire extinguishing agent derived from organic boron compounds suitable for use in controlling and extinguishing fires in metals susceptible to ignition, such as magnesium and its alloys.

2. APPLICABLE SPECIFICATIONS AND OTHER PUBLICATIONS

2.1 The following publications of the issue in effect on date of invitation for bids shall form a part of this specification to the extent specified herein.

2.1.1 Specifications

Military

JAN-P-124	Packaging and Packing for Overseas Shipment; Cans and Pails, Metal
U.S.A.F. Spec. 94-40645	Marking; Exterior, Domestic, and Export Shipment, by Contractors
U.S. Army Spec. 100-2	Marking Shipments by Contractors, Standard Specification for.

Other Publications

Bureau of Supplies
and Accounts Navy Shipment Marking Handbook

ASTM D445-53T Viscosity, Kinematic

"Applied Inorganic
Analysis" - Hillebrand and Lundell (1929)

Scott's Standard Method of Chemical Analysis,
Vol I, pp. 168-9

DeFord: pp. 49-57 (1953 ed.)

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3. REQUIREMENTS

3.1 Composition - The nonaqueous viscous liquid comprising this fire extinguishing agent shall conform to the chemical formula of $(\text{CH}_3\text{O})_3\text{B}\cdot\text{B}_2\text{O}_3$, described by trimethoxyboroxine. When analyzed by the method given under 4.3.2.1 it shall contain a minimum of 58.0% by weight boric oxide calculated as B_2O_3 .

3.2 Viscosity - The sample shall be examined for its viscosity characteristics by the method given under 4.3.2.3 and it shall show a maximum viscosity of 120 centistokes at 0°C .

3.3 Refractive Index - The sample shall have a refractive index of 1.3970 to 1.3980 (n_D^{25}) when tested according to the method given in 4.3.2.3.

3.4 Turbidity - The sample shall contain no visible suspended boric acid crystals and shall exhibit a transmission of not less than 98% in comparison to distilled water when tested in a photoelectric comparator according to the procedure given in 4.3.2.4.

4. SAMPLING, INSPECTION, AND TEST PROCEDURES

4.1 Classification of Tests - The inspection and testing of the fire extinguishing agent of this specification shall be classified as follows:

- (a) Qualification tests: Qualification tests are those tests accomplished on samples submitted for qualification as a satisfactory product.
- (b) Inspection tests: Inspection tests are those tests accomplished on the fire extinguishing agent manufactured and submitted for acceptance under contract.

4.2.1 Qualification Test Sampling Instructions - Qualification test samples shall consist of the following:

- (a) A 1-gallon sample of the material in a sealed moisture-proof container.
- (b) Results of all specification tests.

Samples shall be appropriately identified with the manufacturer's production code number (not experimental number) and any additional information required by the authorizing letter.

4.2.2 Qualification Tests - The Qualification tests shall consist of all the tests specified under Inspection tests.

4.3 Inspection Test Sampling Instructions - When five batches, or less, of the compound are required to fill an order a 2-pound sample shall be taken from each batch and immediately placed in a clean, dry, air- and water-tight container which shall be sealed, marked for identification, and sent to the laboratory for tests. When more than

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five batches are required, the batches shall be grouped together to form not less than three or more than five lots. Each lot shall contain approximately the same number of batches.

A sufficient quantity of the material shall be taken from each batch, in any one lot, to make a 1-gallon composite sample. The sample shall be prepared for testing as described above. A composite sample shall be taken from each lot in a similar manner.

4.3.1 Inspection Tests - The contractor shall furnish all samples and shall be responsible for accomplishing the required tests. When inspection is conducted at the contractor's plant, all inspection and testing shall be under the supervision of the Government Inspector. Contractors not having laboratory testing facilities satisfactory to the Government shall engage the services of a commercial test laboratory acceptable to the Procuring Service. The contractor shall furnish test reports, in duplicate, showing quantitative results for all tests required by this specification, and signed by an authorized representative of the contractor or laboratory, as applicable. Acceptance or approval of material during course of manufacture shall in no case be construed as a guaranty of acceptance of the finished product.

4.3.2. Test Methods - The material shall be subjected to the following tests except that the test described in paragraph 4.3.2.1 shall be required on only every fifth inspection sample. If less than five samples are to be tested, the test shall be run on one sample.

4.3.2.1 Composition - The boric oxide content of the sample shall be determined as follows:

Objective: Determination of boron as boric acid or in a form hydrolyzed to boric acid in aqueous solution.

Scope: Boric acid titrates as a monobasic acid in presence of excess mannitol. The following interfere in the analysis: (a) all cations except alkali metal ions and small amounts of Ca, Sr, and Ba and (b) all anions except Cl^- , Br^- , I^- , NO_3^- , SO_4^{2-} , and small amounts of other anions.

Reference: Scott's Standard Method of Chemical Analysis, Vol I, pp. 168-9; DeFord: pp. 49-57 (1953 ed).

Equipment: Standard; pH meter or auto-titrator (where indicators are not used).

Reagents: Standard acid 0.05N; standard base 0.05N; mannitol, reagent grade; bromocresol green 0.04% or methyl red 0.02%; phenolphthalein 1% or α -naphtholphthalein 0.2%.

Weigh sample into dry weighing bottle

Use sample containing 1-2 mats B or 0.05-0.1 g. unknown

Volatile samples should be handled with care to avoid loss.

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Add sample to 125 ml erlenmeyer flask or 250 ml beaker containing 25-50 ml H_2O ; add 5 drops bromcresol green +7 drops phenolphthalein or 5 drops methyl red +8 drops α -naphtholphthalein.

Sample from HCl titration or hydrolysis reactions may be used.

Use phenolphthalein with bromcresol green or α -naphtholphthalein with methyl red.

Adjust to pH 5-5.5 or bromcresol green or methyl red endpoint.

See HCl titration

Titrate with NaOH to phenolphthalein or α -naphtholphthalein or pH 8.

Usually requires several ml.

Do not add large excess of base.

Add about 2 grams of mannitol and continue titration to phenolphthalein or α -naphtholphthalein endpoint or pH 8.2.

Color should change to acid side if boron is present.

Endpoint may be obscured if too much indicator is used.

Repeat step 5 to stable endpoint.

If sufficient mannitol is added originally, no further titration will be needed.

Note: If titration requires less than 10.0 ml base, analysis is to be repeated using larger sample weight.

Calculations:

$$\frac{(\text{ml std. base}) \times (\text{N of std. base})}{\text{Sample weight in grams}} - \text{mat B/g} \times 0.03482 \times 100 - \%B_2O_3$$

4.3.2.2. Viscosity - The kinematic viscosity of the sample shall be determined using the procedure outlined in ASTM D44 5-5ST except that a temperature of $0^\circ C$ and a Cannon Zhukov closed-type viscometer shall be used. The viscosity of the sample shall be reported in centistokes.

4.3.2.3. Refractive Index - The sample shall be tested for its refractive index in an Abbe double prism refractometer at $25^\circ C$ and reported according to its index $n_{\frac{25}{D}}$, to the fourth decimal place.

4.3.2.4. Turbidity - The sample shall be tested for the suspension of any precipitate by comparing it with dust-free distilled water in a photoelectric comparator such as the Cenco-Sheard Photolometer. The percent of transmission of the sample referred to distilled water at 100% transmission shall be reported.

4.3.3 Rejection and Retest - Materials which have been rejected may be reworked or replaced to correct the defects, and resubmitted for acceptance. Before resubmitting, full particulars concerning previous rejection and the action taken to correct the defects found in the original shall be furnished the inspector. Material rejected after retest shall not be resubmitted without specific approval of the Procuring Service.

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5. PREPARATION FOR DELIVERY

5.1 Application - The packaging, packing, and marking requirements specified herein apply only to direct purchases by or direct shipments to the Government.

5.2 Packaging - Unless otherwise specified in the contract or order the material shall be furnished in 5-gallon pails conforming to Specification JAN-P-124 fitted with a rubber gasket to insure moisture proof closure.

5.3 - Marking and Labeling -

Packages - Each package shall be durably and legibly marked with the following information in such a manner that the markings will not become damaged when the packages are opened:

FIRE EXTINGUISHING AGENT, LIQUID,
BORON TYPE, FOR METAL FIRES

Specification - Ad Interim _____

Stock No. _____

Manufacturers Identification

Designation

Name of Manufacturer

Date of Manufacture

Batch No. _____

CAUTION! REACTIVE LIQUID!
DO NOT OPEN UNTIL READY FOR USE -
DO NOT EXPOSE TO WATER OR HUMID
WEATHER AFTER OPENING - FLUSH
AWAY ALL SPILLED LIQUID WITH
COPIOUS AMOUNTS OF WATER

6. NOTES

Intended Use - The material covered by this specification is intended for use for the purpose of controlling and extinguishing fires in metals such as magnesium, and its alloys, susceptible to ignition in ordinary atmospheres. It must be employed in a stored pressure or pressurizable extinguisher of a design approved for the purpose. It may be used in conjunction with other extinguishing methods such as water-spray and foam where these are needed. No toxic effects are to be expected by its use either from the decomposition of the liquid in the presence of burning metals or from accidental contact of the skin with the material. Evacuation of tightly closed spaces after use of the liquid on fires is to be recommended as well as dilution of the liquid with water where accidental spillage has occurred.

6.1 Provisions for Qualification Tests - The right is reserved to reject any bids on items which have not been subjected to the required tests and found satisfactory. The attention of the manufacturers is called to this provision, and they are urged to request authorization for tests of the material which they propose to offer under this specification. Requests for authorization of tests together with certified test reports showing conformance with all the requirements of this specification, and for information as to the marking and forwarding of samples should be addressed to the Bureau of Aeronautics, Navy Department, Washington 25, D. C.

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6.2 It is to be understood that upon receipt of the letter of authorization, samples shall be furnished at no cost to the Government, and that the manufacturer shall pay the transportation charges to and from the designated point where tests are to be made. In case of failure of the sample or samples submitted, consideration will be given to the request of the manufacturer for additional tests only after it has been clearly shown that changes have been made in the product which the Government considers sufficient to warrant additional tests.

NOTICE: When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.

Custodian: Navy - BUAER

Other interests: Army - S

Air Force

* * *

APPENDIX C
TMB Extinguisher Label

TMB LIQUID FOR MAGNESIUM FIRES

TO OPERATE

1. KEEP EXTINGUISHER UPRIGHT AT ALL TIMES
2. PULL HANDLE LOCKING PIN
3. SQUEEZE HANDLE ONLY FOR LIQUID STREAM
4. DIRECT STREAM ON WHITE FIRE
5. SQUEEZE NOZZLE TO OBTAIN SPRAY PATTERN

AFTER USING

RECHARGE IMMEDIATELY
AFTER USE ACCORDING TO
INSTRUCTIONS WITH RECHARGE KIT.

CHECK GAGE WEEKLY,
NEEDLE MUST REMAIN
IN GREEN RANGE. BE
SURE THAT HOSE AND
NOZZLE ARE NOT OB-
STRUCTED.

Fully Charged Weight 35 lbs.

WARNING! THIS MATERIAL IS FLAMMABLE

KEEP AT TEMPERATURES ABOVE 32° F.

* * *

APPENDIX D
Recharging Kit Contents

1. Pressure Gage - 1/8" IPT male, 1-1/2" diam. face, center back connection, green background for needle indicating recommended operable pressure range of 125-150 psi.
2. "O" ring for neck-cap seal, GR-I rubber or other material resistant to TMB.
3. 2-1/2 gallons of TMB in suitable container capable of moisture-tight re-sealing.
4. Seal wire for locking pin.
5. "O" ring for seal of siphon tube into cap (GR-I rubber if obtainable).
6. "O" ring for overfill preventer tube seal (GR-I rubber if obtainable).
7. Two quarts denatured ethyl alcohol.
8. Recharging instruction sheet.

* * *

APPENDIX E
Instructions for Recharging TMB Extinguishers

READ THESE INSTRUCTIONS COMPLETELY THROUGH BEFORE STARTING

1. The extinguisher should be recharged immediately after any of the contents have been discharged.
2. Relieve any residual pressure by depressing the air valve core.
3. Remove the cap and valve assembly with attached siphon tube after unscrewing the large swivel ring.
4. Any TMB liquid remaining in the extinguisher will react with water (or moisture in the air), to form a white deposit of boric acid, which may plug up small openings in the extinguisher mechanism and interfere with proper operation. The action of boric acid or TMB in contact with the skin is not harmful but it should be wiped off as dry as possible with a dry cloth before washing with water. This will minimize the uncomfortable heat of reaction when water and the TMB are combined.

IMPORTANT!

KEEP IN MIND DURING THE RECHARGING OPERATIONS
THAT THIS LIQUID IS FLAMMABLE

5. Remove the overfill preventer tube and invert to completely empty the extinguisher. (In case the extinguisher contents were only partially discharged, the remaining TMB should be poured into a clean, dry container and sealed up until it can be recharged into the extinguisher.)
6. Hot water may be used to clean out the extinguisher, but if water is used it must be followed by an alcohol rinse to be sure that all water is removed prior to filling with new TMB liquid.
7. To rinse out the whole extinguisher assembly, pour approximately two quarts of denatured alcohol into the shell, replace the cap assembly, shake well, pressurize with a very slight air pressure, and then discharge all the contents. This procedure will clear the valve parts, hose, and nozzle of any residual TMB. Disassemble the extinguisher again and completely dry all parts including the inside of the extinguisher shell, and the valve, hose, and nozzle interiors. The use of an air jet at this point will greatly speed up the drying time.
8. Following this cleaning and drying procedure, replace the "O" rings in the extinguisher shell neck, the overfill tube, and the siphon tube seal with the new "O" rings supplied. Also replace the pressure gage with a new one as supplied. Reassemble the cap unit with its valve, hose, nozzle, and siphon tube intact.

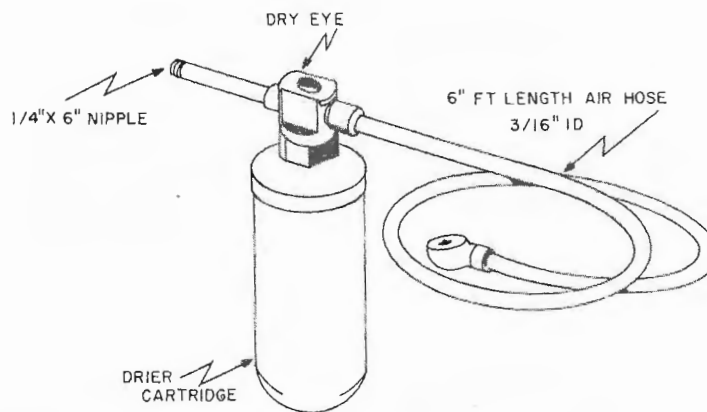


Fig. E1 - Recharging assembly

9. Make sure the overfill preventer tube is in position by firmly seating it all the way in. Refill the extinguisher shell with the TMB liquid supplied, until the liquid can be seen rising in the overfill preventer tube. Again keep in mind that TMB reacts with water and even moisture in the air, therefore, in handling it, use care to prevent contact with moisture. Work in a dry, well ventilated space without any delays. Keep containers of TMB liquid closed, except when actually transferring the liquid.
10. Replace the cap and valve assembly on the extinguisher body and tighten swivel ring.
11. Connect the charging assembly (see Fig. E1) to a source of air at 150-psi pressure. Bleed some air through the system until the "dry eye" shows blue indicating the air is being properly dried. Hold the air chuck to the pressurizing valve and pressurize to 150 psi. When the "dry eye" indicator turns pink in color, the air is no longer being properly dried and the drier cartridge should be replaced with a new one. (In storage between pressurizing operations the "eye" may turn pink from water vapor in the air because it is not sealed up.)
12. Replace lock-pin in valve and secure with lead seal wire.
13. If the weekly inspection shows a loss in pressure, check all the threaded connections at the top of the extinguisher for possible air leaks, using a soap solution. By thus determining the point of leakage, measures can be taken to correct the deficiency.

* * *

APPENDIX F
How to Use the TMB Extinguisher on Magnesium
Fires in Aircraft

Description- This extinguisher contains 2-1/2 gallons of a newly developed liquid agent, trimethoxyboroxine abbreviated as "TMB," for fighting magnesium fires which often occur in crashed or disabled aircraft. The extinguisher is of the stored-pressure type using air pressure to propel the liquid onto the fire. The shut-off valve controlling the liquid flow is in the handle at the top of the unit. The valve in the nozzle at the end of the hose controls only the pattern of discharge of the liquid. Normally this furnishes a straight stream with a maximum range of 25 feet; however, when this handle is fully depressed a spray pattern results having a range of 15 feet.

The viscosity of the TMB material increases very rapidly at low temperatures, therefore this extinguisher must be stored at temperatures no lower than 32°F if it is to be ready for instant use. Although TMB will readily extinguish burning magnesium, it is an unusual fire extinguishing agent in that it itself is a flammable liquid. It burns quietly with a small, light green flame; its flash point is approximately 55°F and the material should be handled accordingly. It also reacts with water, and even moisture in the air, to form a white precipitate of boric acid. Methyl alcohol, denatured ethyl alcohol, and hot water are good solvents to use in cleaning up both TMB and boric acid. TMB on the skin should be wiped off dry with a rag before washing with water. This will avoid the heat generated when the two compounds react. Care should be used in using the extinguisher not to direct the TMB toward the face of other personnel. There are no known toxic products given off during the extinguishing process; however, the white smoke coming from the fire should not be breathed in unnecessarily.

Fire Fighting Tactics- Normally the ignition of magnesium parts in aircraft fires will occur from a burning gasoline spill fire. Only after the blanketing of the gasoline will the fire fighters be able to turn their attention to any burning magnesium. The extinguisher may be carried by either hand with the other hand directing and controlling the nozzle. The burning magnesium should be approached, from upwind if possible, in such a manner as to expose the fire to the straight stream range of the extinguisher. When the fire is within reach, squeeze the valve handle only and direct the liquid stream onto the brilliant white flame.

The liquid will blast out the straight stream tip at full tank pressure when the ring is pulled out and the valve on top of the extinguisher pushed down all the way. The fire fighter can make a smaller amount come out by simply slacking off his grip on this top valve. The liquid can even be dribbled out on small hot spots in the fire by squeezing the valve open very lightly. If he wants a spray pattern to get more coverage in case a large panel is on fire, for instance, the operator holds the extinguisher valve open with one hand and presses the lever on the nozzle with the other. TMB will then squirt out of the spray nozzle. The fire fighter should keep in mind that TMB liquid catches fire quickly and he should be prepared for a possible flare-up when the TMB hits the hot metal fire.

When the TMB liquid hits the hot magnesium it will seethe and froth, quickly taking on the look of a molten, glassy scum over the whole burning surface. By this action the magnesium mass, both solid and molten, is sealed off from oxygen in the air, preventing further combustion. It is important for this reason to cover all burning areas completely with the glassy layer so as to remove all sources of reignition. Underneath this layer the magnesium

will still be red hot so that in using any cooling agent such as water or foam, the crust of TMB must not be penetrated. The foam from the new crash vehicles using foam pumps can be piled up over the whole area without causing difficulty.

There are several things for the operator to remember in fighting a magnesium fire with this new agent. TMB is flammable and when first applied on the fire some will immediately be vaporized, resulting in a sudden flare up of flame and a cloud of white, non-toxic smoke. The size and intensity of this flare up depends on the area of fire covered by the TMB and the direction and force of the wind present. Remember to approach from upwind and for self-protection do not blast TMB at full pressure into a burning mass of magnesium when at close range. This will also prevent pieces of white hot magnesium from being splattered around the general vicinity. Another pointer is to be conservative with TMB after knocking out the initial white fire. Use short bursts or dribbles to get the maximum benefit from the amount of agent that is left, and build up a thick glassy coating over all exposed, burning magnesium surfaces.

Immediately after each use of the extinguisher it should be returned to the fire station for refilling and charging, regardless of how much material has been used. Complete instructions, along with the materials necessary, are provided with each recharge kit.

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