

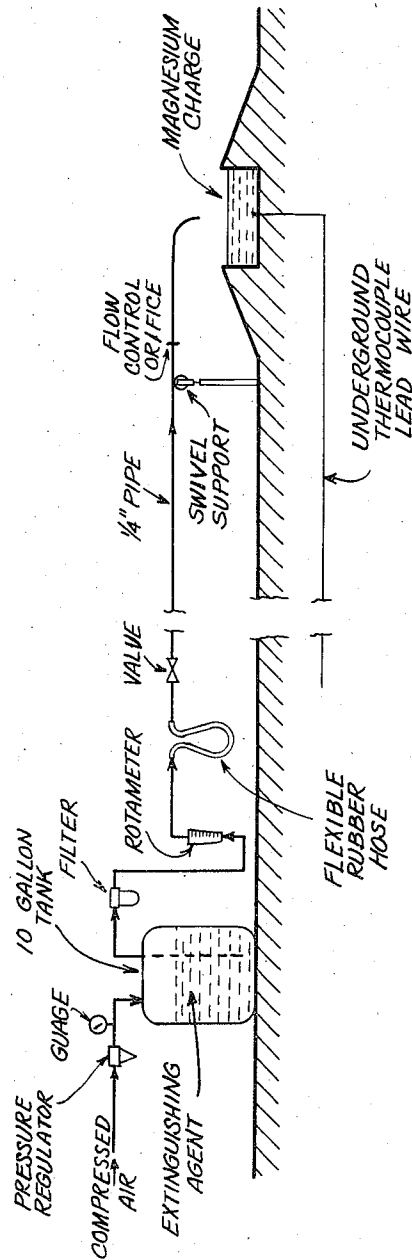
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EXTINGUISHING AGENTS FOR MAGNESIUM FIRES

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EXTINGUISHING AGENTS FOR MAGNESIUM FIRES

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This invention relates to liquid compositions useful for extinguishing magnesium fires and fires of magnesium alloys.

Magnesium and its alloys, as well as other metals, such as calcium, are extremely reactive. Since molten magnesium reacts with water, this most common of extinguishing liquids cannot be used on magnesium fires. Indeed, the reaction between magnesium and water produces hydrogen and the use of water adds the dangers of explosion to those of the magnesium fire. Even exhaustion of available oxygen in the air is not sufficient to extinguish magnesium fires, since nitrogen supports the combustion of the metal with the production of magnesium nitride. Carbon dioxide cannot be used as the extinguishing agent, since it too reacts with magnesium. Carbon tetrachloride similarly is not a suitable extinguishing agent because it reacts violently with the burning magnesium.

Because of the unsuitability of these common extinguishing materials, many of the agents which have been proposed have been solids. These generally depend on mixtures which exclude air mechanically. A mixture of potassium acid sulfate, trisodium phosphate, bauxite, and pumice is said to fuse around the magnesium mass at high temperatures, thereby excluding air. Another extinguishing agent consists of powdered graphite containing a small amount of high boiling liquid, tri(p-tert-butylphenyl)phosphate. The vaporization of the phosphate in the interstices between graphite particles forces out the air, while the graphite provides a cover over the hot metal mass. Solid extinguishing agents are best suited to small fires, where the powder can be applied to the burning surface manually, but are not well adapted to large fires which cannot be closely approached. Since solid extinguishing agents for magnesium must be coated over the entire exposed surface, such agents are usually not suitable for use on large outdoor fires.

The fluid extinguishing agents which have been proposed may be divided into two classes. In the first are those materials which protect the surface magnesium against further progress of the oxidation, but which provide little or no cooling action. An example is boron trichloride liquid or vapor. A second class includes agents with high cooling capacity, but which offer little in the way of protection against further oxidation or ignition. High flash point petroleum or fatty oils fall in this class.

It is accordingly a basic object of this invention to provide fire-extinguishing compositions for magnesium fires which display a high cooling capacity with good protection against additional oxidation of the magnesium and prevention of reignition of the metal.

It is another object of the invention to provide extinguishing agents in the form of liquids which are free-flowing and which can therefore be applied to fires from standard fire-fighting spray nozzles, pumps and similar equipment.

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Other objects and advantages of the invention will in part be obvious and in part appear hereinafter.

The invention accordingly is embodied in a fire-extinguishing agent in liquid form, preferably of a low viscosity so that it is free-flowing like water or light lubricating oil, the agent being a mixture of liquid substances with at least one ingredient from each of two groups, the first group of materials being characterized as non-aqueous organic compounds, which are capable of absorbing large quantities of heat and may be defined as having a high heat absorbing capacity, preferably comparable at least with that of ethyl alcohol, and the second ingredient being selected from a group consisting of halogenated hydrocarbons which have the characteristic that when applied to the burning metal, they will form halogen compounds of the metal, thereby forming a protective coating and even a fusible coating at the burning surface.

The drawing is a diagrammatic representation of the apparatus used in evaluating the compositions of this invention.

Within the class of organic materials having a high heat capacity are a rather large group which includes ethyl and methyl alcohol and similar low molecular weight alcohols, esters of these alcohols and others such as di-2-ethylhexyl phthalate or diisodecyl adipate, fatty acid amides and amines, and high boiling ethers, such as dioctyl ether, which may be mixed with fluid halogenated hydrocarbons such as difluorodibromomethane and monochloromonobromomethane (CH_2ClBr). Fundamentally, the compound having the high heat absorbing capacity is employed for the purpose of providing a rapid cooling of the burning magnesium and it is in a relatively non-viscous solution so that it can be easily applied to the burning mass of material. Since such compounds can be sprayed on the burning metal, their cooling capacity is brought into play most rapidly and they are able to gain access easily to all parts of the burning mass. With the accompanying halogenated hydrocarbons, the application of the material simultaneously produces a protective coating which prevents additional oxidation of the metal.

Preferably the material used as the heat absorber should not react strongly with molten magnesium and it should vaporize freely enough so that its heat absorbing capacity is effectively utilized.

In all fire extinguishing applications, it is desirable to remove heat as quickly as possible, in order to reduce the flammable materials to temperatures below their ignition points. Water, as used in ordinary fire extinguishing, is the most efficient heat absorber, because of its high heat capacity and its very high heat of vaporization. No other common substance approaches its heat of vaporization of 540 calories per gram. Non-aqueous substances which are commonly used as vaporizing liquid extinguishers, such as carbon tetrachloride, derive their effectiveness from the exclusion of oxygen, and from breaking the chain of reactions involved in combustion, rather than from the absorption of heat; carbon tetrachloride, for example, has a heat of vaporization of only 46 calories per gram.

Since water cannot be used as a heat absorber for magnesium, it is necessary to turn to organic liquids with high heat absorbing capacity which do not react violently with the metal. Of the fairly volatile common organic compounds, methanol and ethanol have the highest heat of vaporization, 263 and 204 calories per gram, respectively. Total heat absorbing capacity, however, depends not only on the heat of vaporization, but on the heat capacity of the liquid as well, since this property determines how

much heat is absorbed in raising the liquid from ordinary temperatures to its boiling point. Thus a liquid with a very high boiling point may absorb more heat in attaining that temperature than is required to effect conversion from the liquid to the vapor state. With lower boiling compounds, on the other hand, it is likely that vaporization causes the absorption of more heat than the warming of the liquid to the boiling temperature.

By way of illustration, one pound of ethanol at 25° C. will absorb 16,000 calories while being raised to the boiling point, and 93,000 calories in vaporization, making a total of 109,000 calories. One pound of di-2-ethylhexyl phthalate at 25° C. will absorb an estimated total of 122,000 calories, 98,000 in attaining its boiling point of approximately 386° C., and 24,000 calories in vaporization. In the alcohol, the major part of the heat absorption is in vaporization, and in the phthalate in heating to the boiling point.

Among the extinguishing agents of this invention, the materials of high heat absorbing capacity (group A) which we have shown to be effective as components of magnesium fire extinguishing agents include ethanol, methanol, di-2-ethylhexyl phthalate (DOP), dibutyl phthalate (DBP), diisodecyl phthalate (DIDP), diisodecyl adipate (DIDA), and di(p-tert-butylphenyl)monophenyl phosphate. These group A substances are examples of materials of high heating absorbing capacity, and the invention is not limited to these specific illustrations. For example an alcohol or ester or other organic compound containing a halogen or other substituent may be used because the essential property sought is high heat absorbing capacity.

The heat absorbing substances which have been described are all flammable, although the compounds with high boiling points also have high flash points. One of the functions of the group B, the halogenated hydrocarbon, component of our extinguishing composition is the control of the secondary fire resulting from the ignition of the group A compounds. For example, the secondary fire which results from the application of a mixture of 50% DOP and 50% monochloromonobromomethane (CB) is much more moderate than that which is obtained with DOP alone; in fact as the metal fire extinguishing proceeds and the magnesium is cooled, the presence of CB in the agent causes the secondary fire to be extinguished as well. The presence of CB in this agent has, however, a second function: if the application of extinguishing agent is discontinued when the magnesium temperature is still above the ignition point of approximately 650° C., no reignition occurs. Presumably, some CB reacts with the surface of the burning magnesium to produce a thin impervious protective film of compounds involving magnesium and halogens. In the absence of CB or other halogenated hydrocarbon, reignition of the hot mass takes place; the magnesium oxide and nitride coating which form during combustion is too porous to exclude additional air.

Although we normally use monochloromonobromomethane and difluorodibromomethane as group B substances, other halogenated compounds are also effective.

The performance of magnesium fire extinguishing agents can be expressed in terms of the results of two fire testing techniques. The first test, designed to measure cooling efficiency, determines the quantity of agent necessary to reduce 15 pounds of burning magnesium to a temperature below its ignition point. Since the burning metal generally attains a temperature of about 1050° C., a drop of 440° C. is sufficient to bring the temperature below 650° C. Thus M_{440} is defined as the weight of agent necessary to reduce the temperature of 15 pounds of burning magnesium by 440° C., and therefore represents the quantity required for complete extinguishing of the charge.

In the drawing all elements of the apparatus used for making fine tests are identified.

In the fire test, 15 pounds of magnesium or magnesium alloy are ignited in a cylindrical cavity 11.5 inches in diameter and 6 inches deep, in slightly moistened sand. A chromel-alumel thermocouple, which has been buried in the earth, emerges at the center of the cavity, so that the bimetallic junction is 1.5 inches above the floor of the cavity. The magnesium is ignited by means of an oxy-acetylene torch. As the metal melts and burns, it fills the cavity uniformly. Forced air may be used to bring the metal to a temperature in the neighborhood of 1050° C. more rapidly. When this point is reached, the extinguishing agent is applied in a slow stream or spray at a rate of about one pound per minute. The agent is distributed over the surface of the burning mass by manipulation of the delivery pipe. Because of the rapid heat transfer from the burning magnesium to the agent, the distribution is not critical. The temperature is measured while the agent is applied; from the known rate of application, M_{440} may be calculated.

To test for protection against reignition, an essentially similar procedure is followed, with the exception that application of the extinguishing agent is discontinued when the temperature has fallen to 900° C., which is still 250° above the ignition temperature of magnesium. Furthermore, the sand cavity is lined with a cylindrical steel shell (24 gauge) open at both ends; the additional rigidity is necessary to maintain an approximately constant metal-air interface from test to test. The temperature measurements are continued after application has ceased. If there is adequate protection against reignition, the metal gradually cools. In the absence of such protection, the mass reignites, and the temperature increases. To put the results on a semiquantitative basis, it is convenient to cite the change in temperature twenty minutes after the application is discontinued; this figure is presented as ΔT_{20} . The more negative the value of ΔT_{20} , the more effective is protection against reignition.

In Table I are given M_{440} and ΔT_{20} values for a number of extinguishing agents.

TABLE I

Efficiency of extinguishing agents on magnesium fires

Agent	M_{440} (lb.)	ΔT_{20} (° C.)
50% DIDP in CB	18	-270
50% DIDP in DFDB*	24	-40
100% DIDP	11	+20
50% DOP in CB	20	-200
50% DOP in DFDB*	21	-170
50% DIDA in CB	21	-190
50% Ethanol in CB	22	-170

*DFDB—Difluorodibromomethane.

The secondary fire in each case was much milder when the halogenated hydrocarbon was used. In fire tests where the primary purpose was rapid extinguishing rather than the accumulation of quantitative data, the presence of the halogenated hydrocarbon caused the secondary fire to be self-extinguished as excess extinguishing agent was rapidly added. This does not occur in the absence of halogenated hydrocarbon.

Although all the mixtures of group A and group B compounds which are given in the table are solutions involving equal parts by weight of the two components, the invention is by no means confined to this concentration. The compositions of extinguishing agents tabulated represent compromises between heat absorbing capacity, protection against reignition, and reduction in intensity of the secondary fire. Although a change in the ratio of group A and group B components can place the emphasis on one or another of these properties, solutions covering a wide range of concentrations are very effective fire extinguishing agents for magnesium, as shown in Table II, in which the proportion of denatured ethanol and CB is varied.

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TABLE II

Effect of variation of concentration in ethanol-CB solutions

Agent	M ₄₄₀ (lb.)	ΔT ₂₀ (° C.)
100% Ethanol		+60
90% Ethanol-10% CB	15	-80
50% Ethanol-50% CB	22	-170
30% Ethanol-70% CB	26	
100% CB	>60	+20

It should be noted that the group B halogenated hydrocarbon, CB, when used alone is ineffective as either a cooling or as a protective agent. In the absence of a group A heat absorber, the reaction between magnesium and CB proceeds at so great a rate that the liquid cannot be used as an extinguisher.

Whereas ethanol in the absence of CB has no protective effect, the addition of as little as 10% CB is sufficient to impart some protection, as shown by the change of ΔT₂₀ from +60 to -80° C. When the CB content is increased to 50%, ΔT₂₀ becomes -170° C. M₄₄₀ is lower at the lower concentrations of CB, however, since, in this mixture, it is the alcohol which provides the heat absorbing capacity.

Because the agents of this invention are solutions, it is possible to choose a solid substance from either group A or group B, if the other component is a liquid, and if the solid has the desired solubility in the liquid. For example, Aroclor 1268 (a chlorinated biphenyl marketed by Monsanto Chemical Company) is a solid, but is soluble in CB to the extent of more than 50%. In this case, the compound of high heat absorbing capacity also happens to be a halogenated hydrocarbon. The fire extinguishing agent consisting of 50% Aroclor 1268 in CB has an M₄₄₀ value higher than the agents shown in Table I, but has the advantage that there is no secondary fire, because of the relative non-flammability of the Aroclor. The high M₄₄₀ value is apparently due to the fact that the efficiency of the agent is reduced by the exothermic nature of the reaction between the Aroclor and the magnesium.

It is also possible to improve the effectiveness of the agents by using more than one group A or group B compound. For example, difluorodibromomethane imparts somewhat less protection against reignition than CB, but gives more control over the secondary fire. A mixture of the two gives an overall improvement. Similarly, a combination of group A compounds may be desirable. For storage in cold climates, ethanol is a very desirable component, since it reduces viscosity, while DOP is useful because of its higher flash point. Thus a mixture of the two is indicated.

It will be apparent therefore that the liquid fire ex-

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tinguishing composition may be varied from a small proportion of the organic cooling agent with a large proportion of the halogenated hydrocarbon to a large proportion of the organic cooling agent with a small proportion of the halogenated hydrocarbon. Our tests indicate a range from about 10:1 by weight in the first instance to about 1:10 by weight in the second.

Magnesium, magnesium alloys, e. g., those of aluminum and calcium, and other metals of similar reactivity, all will burn rather violently once they are started. Such fires can be extinguished using the agents described with results paralleling those shown for magnesium. That is, in each case the metal is cooled to a temperature below its ignition point, the fire is converted to a secondary one, and that is readily extinguished.

Though the invention has been described with reference to relatively few examples, it is to be understood that variations thereof may be devised without departing from its spirit or scope.

What is claimed is:

1. A liquid composition useful for extinguishing fires involving burning metal comprising a blend of a first ingredient which is a phthalate ester characterized by its high heat absorbing capacity and a second ingredient which is monochloromonobromomethane, said second ingredient reacting with the metal to form a protective coating to impede further oxidation, the proportions by weight of said ingredients being respectively from about three parts of the first to one part of the second to one part of the first to three parts of the second.

2. A composition in accordance with claim 1 in which said first ingredient is diisodecyl phthalate.

3. A composition in accordance with claim 1 in which said first ingredient is di-2-ethylhexyl phthalate.

4. A liquid composition useful for extinguishing fires involving burning metal comprising a blend of a first ingredient which is a phthalate ester characterized by its high heat absorbing capacity and a second ingredient which is monochloromonobromomethane, said second ingredient reacting with the metal to form a protective coating to impede further oxidation, the proportions by weight of said ingredient being about equal.

5. A composition in accordance with claim 4 in which said first ingredient is diisodecyl phthalate.

6. A composition in accordance with claim 4 in which said first ingredient is di-2-ethylhexyl phthalate.

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