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EXTINGUISHING COMPOSITION

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This invention relates to compositions and methods for extinguishing and preventing light metal fires.

Certain light metals, such as magnesium, aluminum, and sodium, and alloys in which the major portion consists of one or more of these metals, are readily oxidized at elevated temperatures. When, on occasion, these metals become ignited, they burn with an intense, hot flame. Ordinary fire-extinguishing fluids are wholly undesirable to the extent that they may react violently with the hot metal.

It is, therefore, an object of the present invention to provide compositions for extinguishing fires of burning light metals, particularly magnesium- and aluminum-base alloys, which are effective and non-hazardous, and which are easily stored and readily applied to the fire.

The compositions of the invention essentially comprise an aromatic ester of a phosphorus acid, or mixtures of such esters, either with or without other added agents to be described. Typical esters which may be used are aromatic tri-esters of phosphoric acid, especially tri-aryl phosphates such as di-phenyl-mono-(ortho-xenyl) phosphate, tri-(para-tertiary-butylphenyl) phosphate, di-(para-tertiary-butylphenyl) mono-phenyl phosphate, and (4-tertiary-butylphenyl) (phenyl) (ortho-xenyl) phosphate; tri-halo aryl phosphates, e. g. tri-(2,4,6-tri-chlorophenyl) phosphate; aromatic tri-esters of phosphorous acid, e. g. di-(2-xenyl) phenyl phosphite; certain esters of thio-phosphoric acid, such as phenyl di-(meta-tolyl) thiophosphate, and di-phenyl ortho-xenyl thiophosphate, and also such mixed aromatic inorganic phosphorus esters as di-(ortho-xenyl) phosphoric acid di-chloride. Those esters which are liquid are ordinarily preferred because of their ease of application. If desired, the viscosity and pour point of the more viscous liquid esters may be lowered by incorporating therein a small proportion of a tri-alkyl phosphate, such as tri-ethyl or tri-butyl phosphate.

In extinguishing fires with the aromatic phosphorus esters of the invention, the composition is applied directly to the burning metal, usually by sprinkling or spraying it on the fire. The phosphorus compound, on being thus heated, generates vapors which blanket the fire and prevent air from reaching the hot metal. In addition, the extinguisher, because of its high heat of vaporization, tends to withdraw heat rapidly from the burning metal, lowering its temperature to below the ignition point. When large volumes of the composition are applied, there is also a mechani-

cal extinguishing action on the fire due to flooding of the hot metal with cool liquid. In any event, application of the phosphorus ester effectively smothers the blaze without liberating choking, poisonous, or corrosive vapors.

While compositions consisting only of the aromatic phosphorus acid esters described are effective in extinguishing light metal fires, in the case of an intensely hot fire some difficulty may be experienced in that, although the metal fire is smothered effectively, the extinguishing agent itself may become ignited and burn slowly. This difficulty, while not of major significance, may be entirely obviated in any of several ways.

According to one such method, finely-divided carbon, preferably in the form of graphite, is added to the phosphorus acid ester. When such a mixture is applied to a metal fire, the ester quenches the burning metal, as already explained, and the finely-divided carbon, because of its high thermal conductivity, conveys the heat away from the hot mass so rapidly that little if any afterburning of the ester takes place. Particularly effective liquid extinguishing agents may be prepared by mixing a normally liquid aromatic tri-ester of phosphoric acid with a smaller proportion of finely-divided graphite, e. g. so that the latter represents 5 to 50 per cent of the mixture.

In another method of extinguishing large metal fires without afterburning of the phosphorus acid ester extinguishing agent, the latter is applied to the fire as usual and a non-combustible gas which is non-oxidizing toward the phosphorus ester, such as carbon dioxide, sulfur dioxide, nitrogen, ammonia gas, and the like, is also applied to the burning mass either concurrently with, or subsequent to, the application of the extinguishing agent. This gas tends to blanket the fire and to exclude air from the hot metal, preventing ignition of the ester. The desired gas blanket may, in some instances, be generated by adding to the extinguishing fluid a minor proportion of a compound capable of giving off a protective gas of the type described, such as a finely-divided, readily decomposable carbonate, e. g. ammonium bicarbonate.

Aromatic phosphorus esters may also, according to the invention, be employed as one of the ingredients in fire-extinguishing compositions other than those already described. For instance, the ester may be mixed with a larger proportion of finely-divided carbon or graphite, usually such that the mixture consists of 80 to 98 per cent of ground graphite and 2 to 20 per cent of the

aromatic tri-ester of phosphoric acid. The graphite is preferably used in granular form sufficiently fine that the final mixture is free-flowing, and yet not so fine that packing or caking occurs. Optimum results are obtained with graded graphite powder which is all finer than 8-mesh (Tyler standard screen scale), but at least 50 per cent of which is coarser than 200-mesh. If desired, a small proportion of a binding agent, preferably solid asphalt, tar, or pitch, may also be added to the solid extinguishing composition. These solid graphite-phosphorus acid ester extinguishing compositions may be stored for long periods in open containers without deterioration or caking. They are usually applied to a metal fire by spreading them on, as with a shovel. When so used, they effectively quench the fire without liberating dangerous fumes.

While the aromatic phosphorus acid esters have been described principally as fire-extinguishing agents, they are also useful for any purpose where it is desired to prevent the oxidation of heated light metals. Thus, protection may be readily accomplished by covering exposed portions of the hot metal with an atmosphere consisting essentially of a vaporized aromatic ester of a phosphorus acid. For instance, vapors of the esters, when injected into a heat-treating furnace, either with or without the simultaneous addition of a non-oxidizing gas, such as nitrogen, effectively prevent surface oxidation of the metal during the heating operation.

In order to make the present invention more readily understandable, the following illustrative examples are presented, but it is to be understood that they are not intended to limit the scope of the claims in any way:

Example 1

In a test demonstration, a pile of magnesium-base alloy shavings about two inches deep and about twenty-four inches in diameter was ignited, and allowed to burn for several minutes. Liquid di-(ortho-xenyl) mono-phenyl phosphate was then applied to the burning metal through a spray head. The magnesium fire was promptly extinguished but the intense heat of the metal ignited the phosphate smothering agent in small isolated spots. These small flames were easily quenched by applying carbon dioxide to the hot mass.

Example 2

A test substantially identical with that of Example 1 was run with the exception that a small proportion of ground graphite was mixed with the di-(ortho-xenyl) mono-phenyl phosphate. No afterburning occurred subsequent to the application.

Example 3

A fire similar to that in Example 1 was kindled and allowed to burn for a short time. Three shovelfuls of a mixture comprising about 10 per cent by weight of tri-(para-tertiary-butylphenyl) phosphate, about 85 per cent by weight of finely-divided graphite, and about 5 per cent by weight of a 210° F. melting-point coal tar pitch was then sprinkled on the burning mass. The fire was completely extinguished.

Example 4

An open-top steel vaporizing cup containing about 5 cubic centimeters of di-(ortho-xenyl) mono-phenyl phosphate was introduced into a

5-cubic foot capacity heat-treating furnace containing a load of magnesium-base alloy bars. The furnace was then sealed up and maintained at a temperature of approximately 775° F. for 13 hours. The bars, on removal, gave no indication of surface burning. Bars of the same composition subjected to similar heat treatment, except that the phosphorus acid ester protective vapor was omitted, showed considerable surface oxidation.

I claim:

1. A composition for extinguishing burning light metals which consists essentially of a mixture of an aromatic ester of a phosphorus acid and finely-divided carbon.

2. A composition according to claim 1 wherein the carbon is present as graphite.

3. A liquid composition for extinguishing burning light metals which consists essentially of a major proportion of a normally liquid aromatic ester of a phosphorus acid and a minor proportion of finely-divided carbon.

4. A liquid composition for extinguishing burning light metals which consists essentially of 50 to 95 per cent by weight of a normally liquid aromatic tri-ester of phosphoric acid and 5 to 50 per cent of finely-divided graphite.

5. A liquid composition for extinguishing burning light metals which consists essentially of a major proportion of a normally liquid aromatic ester of a phosphorus acid, and a minor proportion of a finely-divided readily decomposable carbonate.

6. A solid composition for extinguishing burning light metals which consists essentially of a major proportion of finely-divided carbon and a minor proportion of an aromatic ester of a phosphorus acid.

7. A solid composition for extinguishing burning light metals which consists essentially of 2 to 20 per cent by weight of an aromatic tri-ester of phosphoric acid and 80 to 98 per cent of finely-divided graphite.

8. A method of preventing the oxidation of light metals at elevated temperatures which comprises covering exposed portions of the hot metal with an atmosphere consisting essentially of a vaporized aromatic ester of a phosphorus acid.

9. A method of extinguishing burning light metals which comprises applying to the burning metal a mixture consisting essentially of an aromatic tri-ester of phosphoric acid and finely-divided carbon.

10. A method of extinguishing burning light metals which comprises applying to the burning metal a stream of a liquid aromatic ester of a phosphoric acid while blanketing the burning mass with an atmosphere of a non-combustible gas which is non-oxidizing toward the said ester.

11. A method of extinguishing burning light metal which comprises applying to the burning metal a stream of a liquid aromatic ester of a phosphoric acid while blanketing the burning mass with an atmosphere of carbon dioxide.

12. A method of extinguishing burning light metals which comprises applying to the burning metal an aromatic ester of a phosphorus acid.

13. A method of extinguishing burning light metals which comprises applying to the burning metal an aromatic tri-ester of phosphoric acid.

14. A method of extinguishing burning light metals which comprises applying to the burning metal a composition which consists essentially

of a mixture of an aromatic ester of a phosphorus acid and finely-divided carbon.

15. A method of extinguishing burning light metals which comprises applying to the burning metal a solid composition which consists essentially of a major proportion of finely-divided carbon and a minor proportion of an aromatic ester of a phosphorus acid.

16. A method of extinguishing burning light metals which comprises applying to the burning metal a solid composition which consists essentially of 2 to 20 per cent by weight of an aromatic tri-ester of phosphoric acid and 80 to 98 per cent of finely-divided graphite.

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