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FIRE EXTINGUISHING AGENT FOR COMBATING METAL FIRES

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ABSTRACT OF THE DISCLOSURE

Fire extinguishing composition of the composition $P(OR)_3 \cdot XP_2O_5$ or $P(OR)_3 \cdot XP_2O_3$ wherein R is an aliphatic hydrocarbon or halogen substituted aliphatic hydrocarbon of 1 to 8 carbon atoms and X is about 0.1 to 2.5 and one of the R's can also be hydrogen.

BACKGROUND OF THE INVENTION

The present invention concerns fire extinguishing compositions which are especially adapted for combating metal fires.

Light metals, such as sodium, potassium, lithium, magnesium, aluminum and some of their alloys, have a substantial affinity for oxygen and as a consequence, if they are not spontaneously combustible are at least highly inflammable and combustible. The combustibility of these metals increases with increase in their surface area so that shavings or grinding dusts such as are obtained in processing such metals are more combustible than larger pieces thereof. In view of the high heat of combustion of these metals considerable heat is evolved during their combustion so that the metal fires spread very rapidly and also easily spread to other combustible materials.

In general metal fires can be extinguished by preventing access of air to the seat of the fire. Of the usual fire extinguishing materials used for this purpose, such as, sand, water, carbon dioxide, carbon tetrachloride and similar substances, only sand can be used for metal fires, as the metals, especially under the influence of high temperatures, react with the other materials and in some instances violently. However, as sand only has a low extinguishing action other substances have been investigated as to their suitability as fire extinguishing agents. For instance, according to U.S. Patent No. 2,787,329 liquid trialkoxy boroxines are sprayed onto the seat of the fire. Such trialkoxy boroxines burn with a green flame with the production of boron oxide which forms an impervious coating on the metal. The use of esters of such acids as boric acid, phosphoric acid or silicic acid, which are based on non-volatile and difficultly reducible oxides in German Patent 729,221 is based on the same principle. All of these fire extinguishing materials, however, have the disadvantage that the actual fire extinguishing substances must first be produced therefrom with occurrence of flames. As a consequence, there is a possibility that these fire extinguishing materials at least at the beginning may contribute to the spread of the fire.

SUMMARY OF THE INVENTION

According to the invention it was found that phosphorus and, if desired, halogen containing reaction products obtained by dissolving of oxides of phosphorus such as P_2O_3 or P_2O_5 in esters of phosphorous acid which, if desired, contains halogen can be used for extinguishing metal fires.

DETAILED DESCRIPTION OF THE INVENTION INCLUDING PREFERRED EMBODIMENTS THERETO

The fire extinguishing compositions according to the invention are of the following composition

$$P(OR)_3 \cdot XP_2O_5$$

$$\begin{matrix} P{-}OH.XP_2O_5, & P(OH).XP_2O_3 \\ | & | \\ (OR)_2 & (OR)_2 \end{matrix}$$

or $P(OR)_3 \cdot XP_2O_3$ in which R represents the same or different aliphatic, cycloaliphatic, saturated or unsaturated hydrocarbons or preferably halogenated hydrocarbons with 1 to 8, preferably, 2 to 3 carbon atoms such as, for example, methyl, ethyl, propyl, butyl, cyclohexyl, chloroethyl, bromoethyl, chloropropyl. X has a value of about 0.1 to 2.5, preferably, 0.25 to 1.25.

In order to prepare the phosphorus and, if desired, also halogen containing reaction products the phosphorus oxide concerned is dissolved in the tri- or di-esters of phosphorous acid. When halogen containing esters of phosphorous acid are employed these preferably should contain fluorine, chlorine or bromine as the halogen. The use of P_2O_5 as the oxide is advantageous in that it is easily obtainable and cheap. Instead of individual oxides and esters, mixture thereof also can be used.

The solutions thus obtained are then heated to temperatures between about 30 and 180° C. to obtain the reaction products employed according to the invention as fire extinguishing agents for metal fires. Depending upon the phosphorus content of such reaction products which are expressed by the value X in the above formulae they are mobile liquids to highly viscous or resin like substances. They are easily dissolved in many common organic solvents, such as, carbon tetrachloride, benzene, fluoro hydrocarbons, hexane, petroleum ether and paraffin oil. In use of the phosphorus and, if desired, halogen containing reaction products according to the invention as a fire extinguishing agents in metal fires, they preferably are sprayed onto the seat of the fire in liquid form with the aid of propellant gases such as nitrogen, carbon dioxide, halo hydrocarbons, such as difluoro dichloro methane. The usual fire extinguishing apparatus such as transportable steel tanks or hand fire extinguishers can be used for the application of the fire extinguishing materials according to the invention. The fire extinguishing materials according to the invention can be used alone or in combination with other known fire extinguishing agents such as light foams or dry extinguishing powders, such as, potassium bicarbonate. Insofar as any of the known fire extinguishing agents which are to be used in combination with the fire extinguishing materials according to the invention for stable solutions or mixtures therewith

such solutions or mixtures can be used for extinguishing metal fires. However, it also is possible to apply the fire extinguishing materials according to the invention and the known extinguishing agents individually but simultaneously to the seat of the fire so as to supplement each other. This procedure is especially expedient when dry fire extinguishing powders are employed in conjunction with the fire extinguishing materials according to the invention.

The phosphorous and, if desired, halogen containing reaction products according to the invention are easily prepared and have good stability on storage. They are not combustible even when subjected to the action of strong flames. Upon heating or contact with flames they foam up with dark discoloration. When they are applied to a burning metal, access of air to the fire is cut off and the fire extinguishes immediately. Depending upon the access of air to the seat of the fire about 0.3 to 1.5 parts by weight of the fire extinguishing material according to the invention per part by weight of burning metal are required to extinguish the fire. During the extinguishing process a protective incombustible layer of foam is formed on the metal surface which prevents rekindling of the metal parts thus coated. The foamed layer also acts as a heat barrier which reduces the heat transfer to such an extent that the ignition of easily combustible material in the neighborhood of the seat of the fire is almost completely precluded. When the fire has been extinguished completely and the metal has cooled down, the foam can be easily removed with compressed air or if no danger is involved with water.

The following examples will serve to illustrate the behavior of the fire extinguishing phosphorus and, if desired, halogen containing reaction products according to the invention in contact with flames and upon heating as well as their good fire extinguishing action.

Example 1

A phosphorous and halogen containing reaction product of the composition $P(O_2H_4Br)_3 \cdot 0.5P_2O_5$, produced in the manner previously described, was applied to an iron sheet and brought into contact with a colorless bunsen burner flame. The originally water clear liquid was discolored thereby over yellow to orange. Upon further contact with the flame a dark colored light foam with high expansion formed which after removal of the flame and cooling was easily removed with water. The substance did not burn during any phase of its contact with the flame.

Example 2

The same phosphorus and halogen containing reaction product employed in Example 1 was applied to another iron sheet and such sheet heated from the other side to read heat (about 600–880° C.) with a bunsen burner. In this instance, also, the liquid first discolored followed by evolution of a white smoke for a short period and thereafter again a dark colored foam with high expansion formed. Again such foam formation was not accompanied by any occurrence of flames.

Example 3.—Extinguishing a magnesium fire

Magnesium ribbon and magnesium shavings which as a whole contained 100 parts by weight of magnesium were piled on a wire netting and heated and ignited with a strong bunsen burner flame. While continuing the application of the bunsen burner a phosphorus containing reaction product of the composition $P(OC_2H_5)_3 \cdot 0.5P_2O_5$ was uniformly sprayed onto the burning magnesium. After about 2–3 seconds a white smoke developed and the surface of the magnesium was coated with a foam like bubbling mass which suffocated the fire after a total of about 6 to 8 seconds. 70 parts by weight of the phosphorus containing reaction product were required to extinguish the magnesium fire.

Example 4.—Extinguishing a magnesium fire

Magnesium ribbon and magnesium shavings which as a whole contained 100 parts by weight of magnesium were piled on a wire netting and heated and ignited with a strong bunsen burner flame. While continuing the application of the bunsen burner a phosphorus containing reaction product of the composition $P(OC_2H_5)_3 \cdot P_2O_5$ was uniformly sprayed onto the burning magnesium. After about one second a white smoke developed and the surface of the magnesium was coated with a foam like bubbling mass which suffocated the fire after a total of about 2 to 3 seconds. 40 parts by weight of the phosphorus containing reaction product were required to extinguish the magnesium fire.

Example 5.—Extinguishing a magnesium fire

Magnesium ribbon and magnesium shavings which as a whole contained 100 parts by weight of magnesium were piled on a wire netting and heated and ignited with a strong bunsen burner flame. While continuing the application of the bunsen burner a phosphorus containing reaction product of the composition $P(OCH_3)_3 \cdot P_2O_5$ was uniformly sprayed onto the burning magnesium. After about one second a white smoke developed and the surface of the magnesium was coated with a foam like bubbling mass which suffocated the fire after a total of about 2 to 3 seconds. 40 parts by weight of the phosphorus containing reaction product were required to extinguish the magnesium fire.

The halogen-containing esters of phosphorous acid required for the preparation of the fire extinguishing compositions according to the invention may be prepared as described in the following examples.

(A) 510 parts by weight of ethylene oxide are introduced within 4 hours into 481 parts by weight of phosphorus trichloride at a temperature of 0° C. The reaction mixture is then slowly warmed to a temperature of 20° C. and the volatile components are distilled off therefrom under a reduced pressure at a bath temperature of 80° C.

The yield of tris-(chloroethyl)-phosphite having a chlorine content of 39.0% and a phosphorous content of 11.0% is 928 parts by weight=98.4% of the theory.

(B) Preparation of tris-(chloropropyl)-phosphite.—Using the procedure described under (A) above, 413 parts by weight of phosphorus trichloride are mixed and reacted with 580 parts by weight of propylene oxide.

The yield of tris-(chloropropyl)-phosphite having a chlorine content of 33.8% and a phosphorous content of 10.15% is 920 parts by weight=98.4% of the theory.

(C) Preparation of tris-(bromopropyl)-phosphite.—Using the procedure described under (A) above, 1,084 parts by weight of phosphorus tribromide are mixed and reacted with 812 parts by weight of propylene oxide. Before separating the volatile components by distillation, small amounts of of yellow-orange precipitate are removed.

The yield of tris-(bromopropyl)-phosphite having a bromine content of 53.6% and a phosphorus content of 6.95% is 1,745 parts by weight=98% of the theory.

The fire extinguishing compositions to be used in accordance with the invention are prepared under the conditions shown in the following table. In each case, phosphorus pentoxide is suspended in the solvent mentioned in the table and the corresponding ester of phosphorous acid is added within 30 minutes while stirring. Then the reaction mixture is heated to the boiling point of the solvent and maintained some time at this temperature.

The preparation of these compounds has been described for the most part in U.S. application Ser. No. 513,530, now U.S. Patent 3,449,475.

Example No.	Ester of phosphorous acid	Moles P_2O_5 per mole ester	Solvent	Reaction temp. in ° C.	Yield in percent of the theory	Content of P and halogen in finished product, wt. percent	
						P	Halogen
1	Tris-(bromoethyl)-phosphite.	0.25	Toluene	110	100	10.55	54.3 bromine.
2	do	0.5	do	110	95	13.4	47.7 bromine.
3	do	1.0	do	111	80	17.0	41.3 bromine
4	do	1.0	Xylene	142–148		22.7	17.3 bromine
5	do	0.25	Benzene	85–86	89	11.6	52.2 bromine.
6	do	0.5	do	84–86	86	13.8	48.5 bromine.
7	do	0.75	do	83–84	93	12.8	45.4 bromine.
8	do	1.0	do	88	90.5	17.0	42.5 bromine.
9	do	2.0	do	85–87		20.7	31.5 bromine.
10	do	1.0	Petrole-um ether.	45–46	97	17.5	41.3 bromine.
11	Tris-(chloroethyl)-phosphite.	1.0	Toluene	113	83	18.65	29.5 chlorine.
12	do	0.25	Benzene	86–87	98	15.2	33.3 chlorine.
13	do	0.5	do	85	94	18.25	30.1 chlorine.
14	do	1.0	do	83–84	100	22.9	25.5 chlorine.
15	do	1.0	Petroleum ether.	45–46	94	22.5	24.9 chlorine.
16	do	5.0		80	99.5	18.0	30.55 chlorine.
17	Tris-(bromoethyl)-phosphite	0.5		80		15.5	47.9 bromine.

Example No.	Ester of phosphorous acid	Moles P_2O_5 per mole ester	Solvent	Reaction temp. in ° C.	Yield in percent of the theory	P Content of finished product, wt. percent	Condition of finished product
18	Triethyl phosphite	0.25	Benzene	78	73	24.8	Colorless, fluid.
19	do	0.5	do	78	98	25.6	Colorless, slightly viscous.
20	do	1	do	78	100	30.1	Light yellowish, viscous.
21	do	2	do	78	95		Yellowish, solid tough resin.
22	do	0.5	Toluene	111	97	23.7	Colorless, slightly viscous.
23	Diethyl phosphite	0.5	Benzene	78	100	29.5	Yellowish, medium viscosity.
24	do	1	do	78		32.0	Yellow, highly viscous.
25	do	0.25	Toluene	111	99	26.7	Fluid.

I claim:

1. A method of combating metal fires which comprises applying a fire extinguishing amount of a reaction product of a composition selected from the group consisting of $P(OR)_3.XP_2O_5$

$$\begin{matrix} P{-}OH.XP_2O_5 \\ | \\ (OR)_2 \end{matrix}$$

$P(OR)_3.XP_2O_3$ and

$$\begin{matrix} P{-}OH.XP_2O_3 \\ | \\ (OR)_2 \end{matrix}$$

wherein R is selected from the group consisting of hydrocarbons of 1–8 carbon atoms and halogenated hydrocarbons of 1–8 carbon atoms and X is a number between 0.1 and 2.5 to the seat of the fire.

2. The method of claim 1 in which X is a number between 0.25 and 1.25.

3. The method of claim 2 in which said reaction product is of the composition $P(OC_2H_5)_3.XP_2O_5$.

4. The method of claim 2 in which said reaction product is of the composition $P(OCH_3)_3.XP_2O_5$.

5. The method of claim 2 in which said reaction product is of the composition $P(OC_2H_4Br)_3.XP_2O_5$.

6. A method of combating metal fires which comprises applying 0.3 to 1.5 parts by weight per part of metal of a reaction product of a composition selected from the group consisting of $P(OR)_3.XP_2O_5$,

$$\begin{matrix} P{-}OH.XP_2O_5 \\ | \\ (OR)_2 \end{matrix}$$

$P(OR)_3.XP_2O_3$ and

$$\begin{matrix} P{-}OH.XP_2O_3 \\ | \\ (OR)_2 \end{matrix}$$

wherein R is selected from the group consisting of hydrocarbons of 1–8 carbon atoms and halogenated hydrocarbons of 1–8 carbon atoms and X is a number between 0.1 and 2.5 to the seat of the fire.

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