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(54) Method for extinguishing difficult to extinguish burning materials.

(57) A very efficient method is proposed for extinguishment of fire involving various dangerous materials hardly fire-extinguishable by conventional methods, such as alkali metal peroxides, aluminum powder, magnesium powder, zinc powder, metallic sodium, metallic potassium, alkyl aluminum compounds and diketene. The method comprises sprinkling, over the fire, a powder having a particle diameter in the range from 5 µm to 5 mm and a pore diameter in the range from 0.1 to 100 µm and composed of porous silica-based particles of which the content of silicon dioxide is at least 80% by weight or porous silica-alumina-based particles of which the total content of silicon dioxide and aluminum oxide is at least 90% by weight. Powder sprinkling mentioned above is preferably followed by spraying water and/or an extinguishment aid which is a Halon compound in the form of liquid at room temperature.

A METHOD FOR FIRE-EXTINGUISHMENT ON HARDLY EXTINGUISHABLE BURNING MATERIALS

BACKGROUND OF THE INVENTION

The present invention relates to a method for extinguishing fire on a hardly extinguishable burning material or, more particularly, relates to a method for extinguishing fire on certain metals, alkali metal peroxides, elementary phosphorus, calcium carbide and the like.

Needless to say, fire on an ordinary combustible or inflammable material takes place when the material is heated in the presence of oxygen or in air to reach the ignition temperature of the respective materials. A most conventional method of extinguishing such fire is to pour water over the burning portion of the combustible material or to flood the burning material with water and to sprinkle a fire-extinguishing agent including sand over the burning material. It is also known, however, that these traditional fire-extinguishing methods are quite ineffective against fires on certain special combustible materials. Examples of such hardly extinguishable combustible materials, referred to as dangerous materials hereinafter, are specified in the Japanese Fire Services Act and classified into Class 1 to Class 6. The traditional fire extinguishing methods are ineffective against the fire on some of these dangerous materials and it is eagerly desired to develop a method by which even the fire on these materials can be rapidly and reliably extinguished.

Following are the natures of the combustion of the dangerous materials of the above mentioned six classes as well as the cautions to be taken in the fire extinguishment on these materials.

(1) Dangerous materials of Class 1

Alkali metal peroxides such as sodium peroxide Na_2O_2 and potassium peroxide K_2O_2 are remarkably unstable and violently and exothermically decomposed when the peroxide is contacted with water producing oxygen gas. Resulting increase in the temperature further accelerates the decomposition of the peroxide to supply an increased volume of oxygen so that the violence of fire is increased so much. Accordingly, flooding of the peroxide with water must be strictly avoided in extinguishing the fire of these alkali metal peroxides. In addition, alkali metal peroxides are capable of decomposing any organic material in contact therewith and at the same time apt to cause a fire accident so that the peroxide must be kept away from any organic materials with utmost care.

It should be noted that most of other conventional fire-extinguishing agents such as carbon dioxide, Halons, powdery phosphates and the like cannot be used in the extinguishment of fire of alkali metal peroxides for some other reasons.

The above-mentioned name of Halons is a nomenclature for a group of halogenated hydrocarbon compounds and a particular Halon compound is designated by a 4- or 5-digit numeral following the name of Halon, of which the first to fifth digits denote the number of carbon atoms, number of fluorine atoms, number of iodine atoms, respectively, in a molecule.

The only method hitherto considered useful for extinguishment of fire of alkali metal peroxides is to sprinkle dry sand in a volume sufficient to cover the burning portion of the material but generally no full effect of fire extinguishment can be obtained. In view of the large amount of sand required for fire extinguishment of a relatively small amount of the peroxide, moreover, it is hardly practical or not possible to keep a stock of a so large amount of sand in a completely dry condition.

(2) Dangerous materials of Class 2

Elementary phosphorus, e.g., yellow phosphorus or red phosphorus, phosphorus sulfide, elementary sulfur and the like are chemically very reactive at elevated temperatures and readily set on fire when they are in contact with air. Powders of certain metals such as aluminum, magnesium, zinc and the like react with steam at a high temperature to produce hydrogen gas. Therefore, the fire of these combustible materials cannot be extinguished by sprinkling or pouring water rather with a result to increase the violence of the fire.

(3) Dangerous materials of Class 3

Alkali metals, e.g., metallic sodium and potassium, calcium carbide and the like belong to Class 3. They must be kept away from water since, when in contact with water, they exothermically produce an inflammable or explosive gas such as hydrogen and acetylene according to the following reaction equations:

$2 Na + 2 H_2O \rightarrow H_2 + 2 NaOH$;

$2 K + 2H_2O \rightarrow H_2 + 2 KOH$; and

$CaC_2 + 2 H_2O \rightarrow C_2H_2 + Ca(OH)_2$.

When these inflammable gases are set on fire by chance, the fire cannot be extinguished by using water as a fire extinguishing agent. Moreover, these materials have reactivity with most of known fire extinguishing agents other than water and therefore cannot be used as a fire extinguishing agent. The only fire extinguishing agent having some effectiveness on these materials is dry sand although the effectiveness thereof is also limited.

Calcium phosphide is also reactive with water or moisture to produce hydrogen phosphide gas which is subject to spontaneous ignition when it is contacted with air to make a chance of fire spreading to any combustible materials nearby so that water can never be used as a fire extinguishing agent on this material.

Calcium oxide is also notorious by the danger of inducing fire on any combustible materials nearby when water is sprinkled or poured thereon due to the large heat evolution although no inflammable gas is produced from calcium oxide per se when it is contacted with water or moisture so that water cannot be used as a fire extinguishing agent when calcium oxide is possibly contacted with water. Other known fire extinguishing agents are also not usable on fire involving calcium oxide due to the high reactivity thereof.

(4) Dangerous materials of Class 4

Alkyl aluminum compounds, such as trimethyl aluminum, triethyl aluminum, tripropyl aluminum and the like, are each a colorless, clear liquid but are highly combustible when they are brought into contact with air. The reaction equations for the combustion of trimethyl aluminum and triethyl aluminum are as follows:

$2\ (CH_3)_3Al + 12\ O_2 \rightarrow 6\ CO_2 + Al_2O_3 + 9\ H_2O$; and

$2\ (C_2H_5)_3Al + 21\ O_2 \rightarrow 12\ CO_2 + Al_2O_3 + 15H_2O$.

Similarly, diketene $C_4H_4O_2$, which is a liquid at room temperature and is widely used as a starting material for the preparation of esters of acetoacetic acid, acetoacetic acid anilide, phenyl methyl pyrazolone, medicines, dyes, germicides, antiseptic agents, stabilizers of synthetic resins and the like, has a very low flash point of 35° C and a boiling point of 127.4° C so that it is liable to be set on fire even when it is heated moderately. At an elevated temperature or under an increased pressure, diketene is highly reactive with atmospheric oxygen according to the reaction equation:

$C_4H_4O_2 + 4\ O_2 \rightarrow 4\ CO_2 + 2\ H_2O$.

Moreover, diketene per se has a strong irritative odor and is strongly lachrymose so that it is frequently responsible for a secondary accident. Due to the insolubility of diketene in water, water cannot be used as a fire extinguishing agent against the fire of diketene rather with an effect of spreading the fire. Most of the conventional powdery fire extinguishing agents are also not usable because of the possible increase of the danger of fire due to the evolution of inflammable gases by the reaction therebetweem.

(5) Dangerous materials of class 6

This class includes fuming sulfuric acid, concentrated sulfuric acid, fuming nitric acid, concentrated nitric acid and the like, each of which may exhibit a strong dehydrating activity when it is contacted with a combustible material such as organic materials with a large quantity of heat evolution so that the combustible material in contact therewith is sometimes set on fire. These strong acids are also liable to emit corrosive and toxic gases.

When fire has taken place with these strong acids included in it, use of water as a fire extinguishing agent should be avoided because dilution of the acid with water produces a large quantity of heat along with evolution of toxic gases. Spreading of the diluted acid is sometimes responsible for a secondary accident. Fire extinguishment with dry sand is also relatively ineffective, so that an unduly large volume of sand has to be sprinkled over the fire.

SUMMARY OF THE INVENTION

The present invention accordingly has an object to provide a novel and improved method for rapid and reliable extinguishment of fire on the above described hardly fire-extinguishable materials based on the principles of fire extinguishment that:

(1) any combustible materials must be kept away from the initial burning site to exhibit the removing effect;

(2) the burning material must be shielded from the source of oxygen supply to exhibit the suffocating effect;

(3) the heat of combusiton must be removed to cool down the burning material to below the ignition temperature to exhibit the cooling effect, when the combustion is effectively retarded; and

(4) the chain reaction of combustion must be suppressed or blocked to exhibit the suppressing effect.

It is of course more effective to perform fire extinguishment by combinig two or more of these principles to exhibit a synergistic effect than to rely on a single principle.

The method of the present invention for fire extinguishment of fire of the above described hardly fire-extinguishable material comprises, in a first aspect thereof, the step of:
sprinkling, over the fire, a powder having a particle diameter in the range from 5 µm to 5 mm and a pore diameter in the range from 0.1 to 100 µm and composed of porous silica-based particles of which the content of silicon dioxide is at least 80% by weight or porous silica-alumina-based particles of which the total content of silicon dioxide and aluminum oxide is at least 90% by weight.

The method of the present invention comprises, in a second aspect thereof, the succesive steps of:

(a) sprinkling, over the fire, a powder having a particle diameter in the range from 5 µm to 5 mm and a pore diameter in the range from 0.1 to 100 µm and composed of porous silica-based particles of which the content of silicon dioxide is at least 80% by weight or porous silica-alumina-based particles of which the total content of silicon dioxide and aluminum oxide is at least 90% by weight; and

(b) spraying water and/or an extinguishment aid which is a Halon compound in the form of liquid at room temperature.

It is preferable that the powder has a true density in the range from 2.1 to 2.5 g/cm^3 and the particles thereof have a surface rendered hydrophobic by a treatment beforehand with an organosilane or an organopolysiloxane.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

When the burning material to be subjected to fire extinguishment according to the inventive method is one or a combination of the alkali metal peroxides, powders of metals, e.g., aluminum, magnesium and zinc, alkali, e.g., sodium and potassium, metals, alkyl aluminum compounds and diketene, the fire can be effectively extinguished according to the above described first aspect of the inventive method.

When the burning material to be subjected to fire extinguishment according to the inventive method is one or a combination of elementary phosphorus, e.g., yellow phosphorus and red phosphorus, phosphorus sulfide, elementary sulfur, calcium carbide, calcium phosphide and calcium oxide or one or a mixture of strong acids such as fuming sulfuric acid, concentrated sulfuric acid, fuming nitric acid, concentrated nitric acid and the like, fire extinguishment can be performed more efficiently according to the second aspect of the inventive method than according to the first aspect.

The silica-based porous powder used in the inventive method should contain at least 80% by weight of silicon dioxide. Though not limitative, a product commercially available under a trade-name of Silton 3S (a natural product occurring in Itoigawa district, Niigata Prefecture, Japan) is quite satisfactory as the starting material. Such a siliceous powder is first calcined and then subjected to a treatment with hydrochloric acid followed by drying and particle size classification prior to use. Silton 3S is not reactive with acids and alkalis, typically, contains 89.1% by weight of silicon dioxide and has a true density of 2.4 g/cm^3, bulk density of 0.3 g/cm^3 and porosity of 70%.

When the porous powder is a silica-alumina-based one, it is essential that the total content of silicon dioxide and aluminum oxide therein is at least 90% by weight. Though not limitative, such a silica-alumina-based powder suitable for use in the inventive method can be obtained by blending and kneading the above mentioned Silton 3S and kaolin with admixture of a small volume of water followed by drying, calcination, pulverization and classification to a range of particle size distribution. Typically, such a powder contains 68% by weight of silicon dioxide and 23% by weight of aluminum oxide and has a true density of 2.5 g/cm^3, bulk density of 0.4 g/cm^3 and porosity of 80%.

The silica-based or silica-alumina-based porous powder used in the inventive method should have a particle diameter of at least 5 µm or, preferably, in the range from 5 µm to 5 mm. A powder having a distribution of particle diameter in the range from 5 µm to 200 µm is suitable for fire extinguishers and a powder having a distribution of particle diameter in the range from 200 µm to 5 mm is suitable for sprinkling by using shovels and buckets. A powder of which the particle diameter is smaller than 5 µm or the true density is smaller than 2.0 g/cm^3 is not suitable for the purpose of the present invention because such a fine or light powder is liable to be scattered or blown away by the violence of vigorously rising flames.

The porous powder should preferably have a pore diameter in the range from 0.1 µm to 100 µm. Powders having a finer pore diameter than 0.1 µm, such as conventional silica gels and alumina gels, are not suitable or rather detrimental against the purpose of fire extinguishment because such a powdery material has high adsorptivity and is sometimes responsible for a temperature increase due to the evolution of heat of adsorption when the powder is brought into contact with the dangerous material in burning.

It is also essential that the porous powder contains impurities in an as low as possible content in order to avoid possible reactions between the impurities and the burning material. Particularly undesirable impurities include iron oxide Fe_2O_3, calcium oxide CaO, magnesium oxide MgO, potassium oxide K_2O and sodium silicate $xNa_2O \cdot ySiO_2$ as well as moisture because these impurities and moisture sometimes react with the burning material to reduce the fire-extinguishing effect of the powder.

It is sometimes advantageous that the porous powder used in the inventive method is imparted with increased moisture-proofness or hydrophobicity and enhanced flowability by a prelimiary surface treatment with an organosilicon compound including organochlorosilane compounds such as methyl chlorosilanes and derivatives thereof and organopolysiloxanes such as methyl hydrogen polysiloxanes and derivatives thereof in order that the porous powder can be sprinkled through a nozzle with the help of gas pressure in a closed vessel.

Halons which are liquid at room temperature can be used as a fire-extibguishment aid in the inventive method. Such an organic halogen compound should not be decomposable at high temperatures of combustion or should not be reactive with ambient gases to exhibit self-extinguishability. Commercial products satisfying these requirements as the fire-extinguishment aid are the below mentioned three chemicals:

Halon 1011 which is monochloromonobromomethane CH_2ClBr;

Halon 1040 which is carbon tetrachloride CCl_4; and

Halon 2402 which is dibromotetrafluoroethane $C_2F_4Br_2$.

These chemicals are available on the market from a plurality of sources.

In the folllowing description of the inventive method, the name of Halon is used to generically designate a fire extinguishing agent including a kind or mixture of these chemicals.

The above mentioned three grades of the Halon products can be graded that Halon 1011 is more effective than Halons 1040 and 2402 relative to the effectiveness when they are used in the inventive method of fire extinguishment. Halon 1040 is a traditional fire extinguishing agent for general purpose but it is banned by laws in recent years from the class of legally authorized fire extinguishing agents because Halon 1040 is liable to be decomposed in flames producing very toxic phosgen $COCl_2$. In the inventive method, however, Halon 1040 can also be used without the problem of producing such a toxic gas because spraying of Halon 1040 is conducted only after the inactive porous powder is sprinkled over the fire to absorb moisture and to cover the burning site.

Following is a description of the process of fire extinguishment on each of different classes of dangerous materials.

1. Extinguishment of fire on alkali metal peroxides, metallic sodium, metallic potassium, aluminum powder, magnesium powder, zinc powder, alkyl aluminum compounds and diketene

When the porous powder is sprinkled over the burning site of the above named dangerous materials, absolutely no chemical changes take place in the powder because the powder is not reactive with the burning material and is in itself heat-resistant and non-combustible. Having porosity, the sprinkled powder acts to absorb the dangerous material in the numberless pores thereof to exhibit the removing effect. When the burning site of the combustible material is fully covered with a layer of the sprinkled powder, furthermore, the burning material is shielded from contacting with the atmospheric air to exhibit the suffocating effect as a result of shielding of the material from the source of oxygen supply.

2. Extinguishment of fire on yellow phosphorus, red phosphorus, phosphorus sulfide, sulfur, calcium carbide, calcium phosphide and calcium oxide

When the porous powder is sprinkled over the burning site of the above named dangerous materials, absolutely no chemical changes take place in the powder because the powder is not reactive with the burning material and is in itself heat-resistant and non-combustible. Having porosity, the sprinkled powder absorbs the moisture which is responsible for the initiation of the fire accident or the burning dangerous material in a molten condition to exhibit the burning-suppressing effect or the removing effect. When the burning site of the combustible material is fully covered by a later of the sprinkled powder, furthermore, the burning material is shielded from contacting with the atmospheric air to exhibit the suffocating effect as a result of shielding of the material from the source of oxygen supply.

When the above mentioned sprinkling of the porous powder is followed by spraying a Halon which is liquid at room temperature or water, the liquid is absorbed in the powder forming the upper portion of the powder layer covering the burning site to increase the suffocating effect by efficiently blocking supply of oxy gen to the burning material below the powder layer. In addition, the sprayed Halon or water is at least partly evaporated by the heat of the burning material so that the burning material is deprived of the heat of vaporization of the Halon or water to exhibit the cooling effect. Thus, the reliability of the fire extinguishment is greatly increased by the synergistic effect when the step of powder sprinkling is followed by spraying of Halon or water.

3. Extinguishment of fire involving strong acids such as sulfuric and nitric acids

When the porous powder is sprinkled over the burning site of the above named dangerous materials, absolutely no chemical changes take place in the powder because the powder is not reactive with the burning material and is in itself heat-resistant and non-combustible. When the combustible material is liquid, the powder absorbs the liquid to exhibit the removing effect and then the suffocating effect is exhibited when the sprinkled powder has formed a covering layer over the burning site to shield the material from supply of oxygen. The powder absorbs the liquid acid to efficiently prevent spreading and flowing away of the acid so that any possible secondary accident due to the spreading acid can be prevented.

When the above described step of powder sprinkling is followed by spraying of a Halon which is liquid at room temperature or water, the suffocating effect is exhibited with further increased reliability along with the cooling effect by depriving the heat of vaporization.

In the following, the method of the present invention is decribed in more detail by way of examples.

Example 1.

A cloth soaked with 5 ml of kerosene was spread on a stainless steel-made dish of 30 cm diameter and 50 g of sodium peroxide Na_2O_2 were put thereon. The cloth wet with kerosene was set on fire. When heated at a high tempeature, the sodium peroxide was burnt violently with orange flames. Thereafter, the fire was extinguished by sprinkling one of different fire extinguishing agents including: (i) a silica-based porous powder having a particle diameter distribution in the range from 5 µm to 500 µm and a pore diameter distribution in the range from 0.1 µm to 10 µm, referred to as the powder A hereinbelow, (ii) a silica-alumina-based porous powder having a particle diameter distribution in the range from 50 µm to 500 µm and a pore diameter distribution in the range from 0.2 µm to 100 µm, referred to as the powder B hereinbelow, and conventional dry sand, referred to as the powder C hereinbelow.

The results of these fire extinguishment tests were that: (i) the fire could be extinguished within 10 seconds by sprinkling 150 g of the powder A over the fire; (ii) the fire could be extinguished within 12 seconds by sprinkling 180 g of the powder B over the fire and; (iii) the fire could be extinguished within 30 seconds by sprinkling 780 g of the powder C over the fire. These results clearly support the outstanding effectiveness of the inventive method not only in respect of the much smaller amount of the sprinkled powder but also in respect of the much shorter time taken for the extinguishment of fire as compared with the conventional method.

Example 2.

The testing procedure was substantially the same as in Example 1 except that sodium peroxide was replaced with the same amount of potassium peroxide K_2O_2 and the powder B was replaced with another silica-alumina-based porous powder having a particle diameter distribution in the range from 50 µm to 5000 µm and a pore diameter distribution in the range from 0.2 µm to 100 µm, referred to as the powder B_1 hereinbelow. When heated at a high temperature, potassium peroxide was melted and violently burnt.

The results of the fire extinguishment tests were that: (i) the fire could be extinguished within 8 seconds by sprinkling 100 g of the powder A over the fire; (ii) the fire could be extinguished within 10 seconds by sprinkling 130 g of the powder B_1 over the fire; and (iii) the fire could be extinguished within 25 seconds by sprinkling 580 g of the powder C over the fire. These results clear ly support the conclusion of the outstanding effectiveness of the inventive method not only in respect of the much smaller amount of the sprinkled powder but also in respect of the much shorter time taken for the extinguishment of fire as compared with conventional methods.

Example 3.

Three sheets of newspaper were spread one on another on a stainless steel-made dish of 30 cm diameter and 50 g of magnesium powder were put thereon. When the newspaper was set on fire, violent burning of the magnesium powder started after 1 to 1.5 minutes from ignition. Thereafter, 50 g of a silica-alumina-based porous powder having a particle diameter distribution in the range from 50 to 1000 µm and a pore diameter distribution in the range from 0.2 µm to 100 µm, referred to as the powder B_2 hereinbelow were sprinkled over the fire so that the fire could be extinguished within 25 seconds without making any noise.

For comparison, 290 g of the powder C used in Example 1 were sprinkled over the fire so that the fire could be extinguished within 30 seconds making some noise for a while immediately after sprinkling of the powder. The magnesium powder, however, was still in a condition of red heat in the core portion of the blocked pile of the powder to cause further temperature elevation on the surface layer so that the file could be completely extinguished only by using an additional amount of the fire extinguishing agent.

Example 4.

As a preliminary test, 30 ml of trimethyl aluminum $(CH_3)_3Al$ were taken in a metal-made vessel and left standing there until spontaneous combustion took place. The fire could easily be extinguished by sprinkling 40 g of the powder B_2 used in Example 3 over the fire. Then, a blend of 50 ml of trimethyl aluminum and 50 ml of liquid paraffin was taken in the same metal-made vessel as above and left standing until spontaneous combustion took place. The fire could be extinguished within 60 seconds by sprinkling 30 g of the same powder B_2 as above over the fire.

On the other hand, the fire in a similar test for comparison failed to be extinguished by sprinkling 520 g of the same powder C as used in Example 1.

Example 5.

A fire extinguishment test of diketene was undertaken by sprinkling 40 g of the powder A used in Example 1 over 50 ml of diketene taken in a stainless steel-made small vessel after 20 seconds of preliminary uncontrolled burning so that the fire could be extinguished within 15 seconds without making any noise due to boiling of the liquid. The temperature of diketene left in the vessel after extinguishment did not exceed 55 °C.

The fire in a similar test for comparison could be extinguished only after 25 seconds by sprinkling 270 g of the same powder C as used in Example 1 making a noise of boiling liquid at the initial stage of powder sprinkling. The temperature of diketene left after extinguishment in the vessel had reached 60.5 °C.

Example 6.

A stainless steel-made vessel having an inner diameter of 10 cm and a depth of 6 cm was charged with 50 g of calcium carbide to which 30 ml of water were poured to evolve acetylene gas. After 20 seconds of uncontrolled burning by ignition of acetylene gas, the fire was extinguished by undertaking one of the following four testing ways.

Test 1. The fire could easily be extinguished within 30 seconds by sprinkling 100 g of the powder A used in Example 1 using a metal-made spoon.

Test 2. The fire could easily be extinguished within 30 seconds by sprinklings 60 g of the powder A followed by spraying of a small volume of Halon 1011.

Test 3. The fire could be extinguished within 35 seconds by sprinklings 120 g of the powder B_1 used in Example 2.

Test 4. The fire failed to be extinguished even after 90 seconds by sprinkling 650 g of the powder C used in Example 1.

As is understood from the above given results of the tests, the fire of acetylene over calcium carbide could hardly be extinguished by sprinkling a large amount of conventional dry sand while the fire could easily be extinguished according to the inventive method by using a very small amount of the fire extinguishing agent which could be further reduced when sprinkling thereof is followed by spraying of a small volume of a liquid Halon.

Example 7.

A stainless steel-made vessel having an inner diameter of 10 cm and a depth of 6 cm was charged with 50 g of calcium phosphide to which 30 ml of water were poured to evolve phosphine gas. After 20 seconds of uncontrolled burning by ignition of phosphine gas, the fire was extinguished by undertaking one of the following three testing ways.

Test 1. The fire could be extinguished within 15 seconds by sprinklings 80 g of the powder A used in Example 1 using a metal-made spoon.

Test 2. The fire could be extinguished within 20 seconds by sprinkling 100 g of the powder B_1 used in Example 2.

Test 3. The fire could be extinguished within 30 seconds by sprinkling 550 g of the powder C used in Example 1.

As is understood from the above given results of the tests, the fire of phosphine over calcium phosphide could be extinguished only by sprinkling a large amount of conventional dry sand taking an unduly long time while the fire could easily be extinguished according to the inventive method by using a very small amount of the fire extinguishing agent.

Example 8.

Three sheets of cloth soaked with 5 ml of kerosene were spread one on another on the bottom of a porcelain vessel having an inner diameter of 10 cm and a depth of 8 cm and 100 g of calcium oxide were put thereon, to which 30 ml of water were poured to cause foaming leading to spontaneous combustion. After 10 seconds from the ignition, the fire was extinguished by undertaking one of the following three testing ways.

Test 1. The fire could be extinguished within 20 seconds by sprinkling 120 g of the powder A used in Example 1 using a metal-made spoon.

Test 2. The fire could be extinguished within 23 seconds by sprinkling 150 g of the powder B_1 used in Example 2.

Test 3. The fire could be extinguished within 45 seconds by sprinkling 900 g of the powder C used in Example 1.

As is understood from the above given results of the tests, the fire caused by calcium oxide contacting with water could be extinguished only by sprinkling a large amount of conventional dry sand taking an unduly long time while the fire could easily be extinguished according to the inventive method by using a very small amount of the fire extinguishing agent within an outstandingly short time.

Example 9.

A cloth soaked with 10 ml of kerosene was spread on a stainless steel-made dish having a diameter of 30 cm and 20 g of sawdust were put thereon. Then, 50 g of fuming nitric acid were dripped to the pile of sawdust so that nitrogen dioxide gas NO_2 was evolved along with browning of the sawdust. Thereafter, the cloth wet with kerosene was set on fire so that the sawdust wet with fuming nitric acid started to burn. The fire was extinguished by undertaking one of the following three testing ways.

Test 1. The fire failed to be extinguished by sprinkling 40 g of the powder A used in Example 1 even after 90 seconds from the powder sprinkling. The condition of burning could hardly be altered when the powder sprinkling was followed by spraying of a Halon while smoking was ceased and the fire could be extinguished when water was sprayed thereto following spraying of the Halon.

Test 2. The fire could be extinguished within 1 minute when sprinkling of 110 g of the powder A was followed by spraying of water.

Test 3. When 830 g of the powder C used in Example 1 were sprinkled over the pile of the burning sawdust, smoking could be subdued about to disappear after 2 minutes. However, brown smoke again rose by shuffling the pile. Despite the use of a much larger amount of powder, the powder C is less effective to extinguish the fire than the powder A.

The above described results of tests clearly indicate that the fire taking place from fuming nitric acid contacting with an organic material can be easily extinguished according to the inventive method with an outstandingly small amount of the powder within a short time along with prevention of any secondary hazard due to spreading of nitric acid.

Example 10.

A cloth soaked in 10 ml of kerosene was spread on a stainless steel-made dish having a diameter of 30 cm and 20 g of sawdust were put thereon. Then, 50 g of fuming sulfuric acid were dripped to the pile of sawdust so that blackening of the sawdust took place. Thereafter, the cloth wet with kerosene was set on fire so that the sawdust wet with fuming sulfuric acid started to burn. The fire was extinguished by undertaking one of the following two testing ways.

Test 1. The fire could be extinguished within 15 seconds by sprinkling 70 g of the powder A used in Example 1 over the fire.

Test 2. When the 400 g of the powder C used in Example 1 were sprinkled over the pile of the burning sawdust, the fire could be extinguished within 30 seconds though leaving a possibility of restarting of combustion depending on conditions.

To summarize, the present invention provides several advantages that:

(1) the fire on any hardly fire-extinguishable materials can easily be suppressed and extinguished;

(2) a possibility of fire extinguishment is obtained with reliability and by using an outstandingly small amount of the fire extinguishing agent within a short time as compared with fire extinguishment by using conventional dry sand;

(3) different from conventional dry sand, the fire extinguishing agent proposed in the invention is suitable as a filling in a powder-ejecting fire extinguisher or a fire extinguishment equipment;

(4) when the powdery fire extinguishing agent used in the inventive method is imparted with hydrophobicity, the fire extinguishing power of the powdery agent is freed from decrease by absorption of water or moisture during storage; and

(5) because the powdery fire extinguishing agent used in the inventive method is composed of a simple constituent containing very little impurities and not including unduly fine particles, the powder sprinkled can be easily disposed without problems of environmental pollution and, in addition, the efficiency of fire extinguishment by use thereof can be further enchanced with powder sprinkling is followed by spraying a Halon which is liquid at room temperature or water to exhibit the cooling effect.

Claims

1. A method for extinguishment of fire on a hardly fire-extinguishable material which comprises the step of:
sprinkling, over the fire, a powder having a particle diameter in the range from 5 µm to 5 mm and a pore diameter in the range from 0.1 to 100 µm and composed of porous silica-based particles of which the content of silicon dioxide is at least 80% by weight or porous silica-alumina-based particles of which the total content of silicon dioxide and aluminum oxide is at least 90% by weight.

2. The method for extinguishment of fire as claimed in claim 1 wherein the powder has a true density in the range from 2.1 to 2.5 g/cm^3.

3. The method for extinguishment of fire as claimed in claim 1 wherein the powder has a surface rendered hydrophobic by a treatment with an organosilane compound or an organopolysiloxane compound.

4. The method for extinguishment of fire as claimed in claim 1 which further comprises the step of, subsequent to sprinkling of the powder, spraying water and/or an extinguishment aid which is a Halon compound in the form of liquid at room temperature.

5. A method for extinguishment of fire on a hardly fire-extinguishable material selected from the group consisting of alkali metal peroxides, aluminum powder, magnesium powder, zinc powder, metallic sodium, metallic potassium, alkyl aluminum compounds and diketene which comprises the step of:
sprinkling, over the fire, a powder having a particle diameter in the range from 5 µm to 5 mm and a pore diameter in the range fro 0.1 to 100 µm and composed of porous silica-based particles of which the content of silicon dioxide is at least 80% by weight or porous silica-alumina-based particles of which the total content of silicon dioxide and aluminum oxide is at least 90% by weight.

6. The method for extinguishment of fire as claimed in claim 5 wherein the powder has a true density in the range from 2.1 to 2.5 g/cm^3.

7. The method for extinguishment of fire as claimed in claim 5 wherein the powder has a surface rendered hydrophobic by a treatment with an organosilane compound or an organopolysiloxane compound.

8. The method for extinguishment of fire as claimed in claim 5 which further comprises the step of, subsequent to sprinkling of the powder, spraying water and/or an extinguishment aid which is a Halon compound in the form of liquid at room temperature.

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Application Number

EP 88 11 5453

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	CHEMICAL ABSTRACTS, vol. 99, no. 16, 17th October 1983, page 141, abstract no. 125028r, Columbus, Ohio, US; & JP-A-58 69 584 (ASAHI ASBESTOES CO., LTD) 25-04-1983 * Abstract *	1,2,5,6	A 62 D 1/00
Y	IDEM	3,7	
Y	US-A-3 830 738 (A.G. COTTRELL) * Column 1, lines 33-51; column 4, line 34 - column 5, line 6; column 5, lines 40-71 *	3,7	
X	CHEMICAL ABSTRACTS, vol. 87, no. 24, 12th December 1977, page 126, abstract no. 186709n, Columbus, Ohio, US; & SU-A-423 323 (ALL-UNION SCIENTFIC-RESEARCH INSTITUTE OF FIRE PREVENTION) 05-08-1977 * Abstract *	1-8	
X	US-A-4 008 170 (B.D. ALLAN) * Whole document *	1,2,5,6	TECHNICAL FIELDS SEARCHED (Int. Cl.4) A 62 D
A	US-A-4 173 538 (C.L. HERBLINE) * Column 3, line 1 - column 5, line 42; claims *	1-8	
A	GB-A-1 205 136 (U.K. ATOMIC ENERGY AUTHORITY) * Whole document *	1,2,5,6	
A	US-A-2 969 116 (A.B. GUISE) * Whole document *	1-8	

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	30-11-1988	FLETCHER A.S.

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A	US-A-3 055 435 (W.R. WARNOCK et al.) * Whole document * -----	1-8	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)

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