Experimental study on fires extinguishing properties of melamine phosphate powders

SONG Fudang*, DU Zhiming, CONG Xiaomin, ZHAO Linshuang, YAN Ye, LI Linming

State Key Laboratory of Explosion Science and Technology, Beijing Institute of Technology, Beijing100081, China

Abstract

A new type of multipurpose dry powders (MP dry powders) with melamine phosphate as extinguishing component was prepared by using the ball-milling method. The main physical properties of MP dry powders were tested, and the extinguishing experiments including wood crib fire tests and pool fire tests were conducted to study the extinguishing properties of MP dry powders comparing with commercial ordinary ammonium phosphate dry powders. The thermal decomposition properties of melamine phosphate were studied through thermogravimetric (TG) and differential scanning calorimetry (DSC). The results show that the bulk density of MP dry powders is lower than the required value, and the other main physical properties accord with the demands of Chinese Standards. MP dry powders have higher extinguishing effectiveness on wood crib fire tests and pool fire tests than that of commercial ordinary ammonium phosphate dry powders. Finally, the extinguishing mechanisms were discussed on the base of thermal decomposition properties of melamine phosphate.

Keywords: dry powders; melamine phosphate; wood crib fires tests; pool fires tests; thermal decomposition

1. Introduction

Multipurpose dry powders have been widely used in the portable fire extinguisher and the fixed fire extinguishing system because of its high extinguishing effectiveness, wide range of applications, safety and

* Corresponding author. Tel.:18811313341.
E-mail address: songfudang@126.com
environmentally friendly, etc [1]. The extinguishing mechanism is complicated especially for Class A fires, previous studies point to some mechanisms such as thermal cooling, physical covering and any type of mass-transfer inhibition, etc [2].

The effectiveness of dry powders depends on its components and particle size. The extinguishing components, which can decompose and/or vaporize in the flame, are the core element of dry powders [3]. In previous studies, many experts and scholars have developed some new extinguishing components, for example, Hu Bing-cheng [4] made a new type of dry powders with phosphate ore(mainly contain calcium phosphate and calcium carbonate) as extinguishing component, and its extinguishing effectiveness was higher than sodium bicarbonate powders. Wang Li [5] made a new superfine dry powders with magnesium hydrate as extinguishing component, its fire-extinguishing time was shorter than ammonium phosphate powders. William [6] made a new superfine dry powders with boracic acid as fires extinguishing component, and it has higher extinguishing effectiveness on Class B fires. However, all of these new extinguishing components can’t extinguish Class A fires. For Class A fires, one must consider both flaming and smoldering, the powders or its decomposition must cover the burning surface to extinguish smoldering.

Melamine phosphate is a kind of fires retardant with nitrogen and phosphorus as the main compositions, it would release non-flammable gas such as steam and ammonia when heated, and the phosphorus would make the base material carbonization to form carbonized layer [7]. In extinguishing fires, the non-flammable gas would cool the burning surface and dilute the oxygen of burning zone. The carbonized layer covered on the solid surface would inhibit any type of mass-transfer. So we selected melamine phosphate as extinguishing component to prepare a new type of multipurpose dry powders, its main physical properties and the extinguishing properties were tested through experiments. In addition, we discussed the extinguishing mechanism on the base of thermal decomposition properties of melamine phosphate.

2. Experimental

2.1. Instruments and materials

Pot-shaped mill (GQM-10/15-4); High-speed mixer (GH-10A); Laser Particle Size Analyzer (BT-9300H); Asphalt penetration; Temperature monitor (MV100); Mettler Toledo-synchronous thermal analyzer; Melamine phosphate (industrial grade); Talc powders, Atlapulgite, Hydrophobic silica (chemical grade); Silicone oil (Special oil bath level); Acetone (analytical reagent); Commercial ordinary ammonium phosphate powders (ammonium dihydrogen phosphate content 50%).

2.2. Preparation of melamine phosphate powders (MP dry powders)

Adding melamine phosphate, talc powders, atlapulgite and hydrophobic silica into pot-shaped mill in order, the mixture can be mixed evenly after 15 min under the condition of 200r/min. The mixed powders was modified in high-speed mixer by the following steps to reduce hygroscopicity and caking properties. First, spraying the silicone oil diluted with acetone to the surfaces of mixed powders and stirring the powders of 5 min under the condition of 50 ℃ and 1000 r/min, then the powders were modified of 40 min under the condition of 70 ℃ and 800 r/min, when they cooled down and solidified, the mixed powders (MP dry powders) can be used in extinguishing experiments.

2.3. Physical properties of melamine phosphate powders (MP dry powders)

The main physical properties of MP dry powders including bulk density, moisture content, hygroscopic rate, noncaking properties and effective discharge rate were tested according to the methods prescribed by GB4066.2-2004 [8]. The results are shown in Table1.
Table 1. Results of physical properties tests.

<table>
<thead>
<tr>
<th>Items</th>
<th>Technical requirements</th>
<th>Mp dry powders</th>
</tr>
</thead>
<tbody>
<tr>
<td>bulk density / (g/ml)</td>
<td>≥0.85</td>
<td>0.58</td>
</tr>
<tr>
<td>moisture content /%</td>
<td>≤0.20</td>
<td>0.09</td>
</tr>
<tr>
<td>hygroscopic rate /%</td>
<td>≤2.00</td>
<td>1.02</td>
</tr>
<tr>
<td>noncaking properties (penetration) /mm</td>
<td>≥16.0</td>
<td>35.6</td>
</tr>
<tr>
<td>effective discharge rate /%</td>
<td>≥90</td>
<td>92</td>
</tr>
</tbody>
</table>

The bulk density mainly depends on the density of raw material and the particle size of powders, the density of melamine phosphate is low and the particle size of MP dry powders is small, so the bulk density of MP dry powders is lower than the required value which is advantageous to extinguish fires. The lower the bulk density, the smaller the resistance, so the penetration value is greater than the required value. The moisture content and hygroscopic rate are lower than the required values mainly due to the water absorbency of melamine phosphate is low and the powders are modified by the silicone oil and hydrophobic silica. From the above results, it can be concluded that MP dry powders have good storage stability and its extinguishing properties can be kept for a long time.

Particle size distribution is one of the main physical properties and it is also the main factor influencing the extinguishing properties. All particles of an agent below a unique limiting size completely decompose and/or vaporize in the fires and have the same extinguishing effectiveness, however, particles below the limit are easy to loss during eruptions, hence, it appears that there is an optimum particle size distribution for maximum extinguishing effectiveness [9]. The size distribution of MP dry powders was measured by using Laser Particle Size Analyzer (BT-9300H). The results are shown in Fig. 1.

Fig. 1 shows that the average diameter of MP dry powders is 0.026mm (D_{50}=0.026mm), and the diameter of maximum particles is 0.200 mm (D_{100}=0.200 mm), they meet the requirements of Chinese Standards: D_{50}≤0.040mm, D_{100}≤0.250 mm. Particles larger than 44 μm account for 28.26%, these particles of powders dispensed from nozzles drag smaller ones to, and into, a fires to improve the extinguishing effectiveness [9].

Fires extinguishing apparatuses are given in Fig. 2. The supply quantity was determined using the portable fire-extinguishers through many times tests. The definition of fire-extinguishing time was different. For wood crib fires,
the fires-extinguishing time referred to the time from dispensing powders to the temperature of wood crib center (2-thermocouple) dropped to 200 °C. For pool fires, the fires-extinguishing time referred to the time from dispensing powders to the temperature above the pool (1-thermocouple) dropped to 200 °C.

For wood crib fires, the pieces of wood crib are 15 mm×15 mm×150 mm, a total of 4 layers, the metal holders are 30 cm, and the size of the pool to ignite wood crib is 20 cm×20 cm×6 cm. The volume of fuel (n-heptane) was 100ml in each test. After the fuel burning out, the wood crib would free burn about 1 min as appropriate, then we began to dispense the powders. The extinguishing equipment was portable fire extinguisher of 500 g, the driver gas was compressed nitrogen gas, its pressure was 1.2 MPa, the distance from the nozzle to the center of wood crib was more than 100 cm when the operators begin to dispense the powders, then he/she can attack the fires from the front, the face and two sides. The temperature changes of wood crib fires tests were monitored by K-thermocouple instruments as shown in Fig. 2 (a).

For pool fires, the size of the pool is 20 cm×20 cm×6 cm, and the volume of fuel (n-heptane) was also 100 ml in each test. We began to extinguish fires after the combustion become stable (about 60 s). There were four K-thermocouple instruments above the fuel at 5 cm intervals to monitor the temperature changes of pool fire tests as shown in Fig. 2 (b).

3. Results and discussion

3.1. Wood crib fire tests

For wood crib fires, the experimental results are shown in Table 2. We can see that the extinguishing effectiveness of MP dry powders is higher than that of commercial ordinary ammonium phosphate powders, its supply quantity and fire-extinguishing time are less than that of commercial ordinary ammonium phosphate powders. The supply quantity is decreased to 50%-60% and the extinguishing time is reduced by 56%.

Fig. 3 shows the temperature curves of wood crib fire tests. In free burning phase, the temperature of 1-thermocouple is lower than that of other thermocouples because the fuel burn out and it is only affected by radiant heat from the burning wood crib. When we begin to dispense the powders, the powders interact with the flames and the flames disappear quickly, so the temperatures of 3-thermocouple and 4-thermocouple drop rapidly to 400 °C. The falling rate of temperature become slower below 400 °C due to the smoldering, but the falling rate of wood crib applying MP dry powders is faster than that of wood crib applying commercial ordinary ammonium phosphate powders (especially 2-thermocouple), this is mainly because the particles of MP dry powders are smaller and its bulk density is lower, so more particles reach the surfaces of the wood crib and form a uniform coating on it [10].

Fig. 4 is the video capture of wood crib fire tests with MP dry powders. From the picture it can be seen that the flame was inhibited after dispensing MP powders, when the flame was extinguished, it became easier for MP dry powders to reach the surfaces of wood crib. Finally, a crib fires, which have both flaming and smoldering contributions, was extinguished.
Table 2. Experimental results of wood crib fires tests.

<table>
<thead>
<tr>
<th>Fires model</th>
<th>Types</th>
<th>supply quantity /g</th>
<th>extinguishing time /s</th>
<th>Reburn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood crib fires</td>
<td>MP dry powders</td>
<td>40.0–45.0</td>
<td>46.0</td>
<td>No</td>
</tr>
<tr>
<td></td>
<td>Commercial ordinary ammonium phosphate powders</td>
<td>75.0–80.0</td>
<td>104.0</td>
<td>No</td>
</tr>
</tbody>
</table>

Fig. 3. (a) Temperature curves of wood crib fire tests with MP dry powders; (b) Temperature curves of wood crib fire tests Commercial ordinary ammonium phosphate powders.

3.2. Pool fire tests

For pool fires, the experimental results are shown in Table 3. We can see that the fire-extinguishing time of two types dry powders is similar, however, the supply quantity of MP dry powders is decreased to 50%–71%, hence, MP dry powders also have higher extinguishing effectiveness than that of commercial ordinary ammonium phosphate powders on pool fires.

Table 3. Results of pool fires tests.

<table>
<thead>
<tr>
<th>Fires model</th>
<th>Types</th>
<th>supply quantity /g</th>
<th>extinguishing time /s</th>
<th>Reburn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pool fires</td>
<td>MP dry powders</td>
<td>20.0–25.0</td>
<td>17.5</td>
<td>No</td>
</tr>
<tr>
<td></td>
<td>Commercial ordinary ammonium phosphate powders</td>
<td>35.0–40.0</td>
<td>19.7</td>
<td>No</td>
</tr>
</tbody>
</table>

Fig. 5 shows the temperature curves of pool fire tests. In preburn phase, the temperature curves are unstable because of combustion instability, hence, we begin to extinguish fires after the combustion become stable (about 60 s). The flames were inhibited after dispensing two type of dry powders, so the temperature above the pool (1,2,3,4-thermocouples) drop rapidly to 200 °C. The temperature falling rate become slower below 200 °C because the pool
release heat to the surroundings continually, and the temperature difference between the pool and the surroundings become smaller.

![Temperature curves of pool fire tests with MP dry powders](image1)

**Fig. 5.** (a) Temperature curves of pool fire tests with MP dry powders; (b) Temperature curves of wood crib fire tests Commercial ordinary ammonium phosphate powders.

Fig. 6 is the video capture of pool fire tests with MP dry powders. From the picture it can be seen that the flames shifted and its height increased at the instant of dispensing Mp dry powders, this is due to the driver gas drove the surrounding air into the fires and the combustion was reinforced in the moment [11]. As we continue to dispense the powders, the flame roots were cut off from the pool, and the pool fires extinguished quickly. Finally, the powders formed a layer above the pool and it can’t reburn again.

![Video capture of pool fires tests with MP dry powders](image2)

**Fig. 6.** Video capture of pool fires tests with MP dry powders.

### 3.3. Extinguishing mechanism discussion

Melamine phosphate is a kind of environmental friendly fire retardant, its fire-retardant mechanisms have been studied by many experts and scholars. This article referred to the previous studies of fires-retardant mechanism and discussed the extinguishing mechanism of MP dry powders. The TG-DSC curves of Melamine phosphate was obtained by using Mettler Toledo-synchronous thermal analyzer at a heating rate (10 °C/min) from 50 °C to 800 °C in air atmosphere.

TG-DSC curves of melamine phosphate are presented in Fig. 7. It can be seen that Melamine phosphate start to decompose at about 250 °C, it turns into melamine pyrophosphate and releases steam and a small amount of melamine. The weight loss rates increase at about 400 °C due to melamine pyrophosphate transform into (PNO)x inorganic cross-linked polymer and release steam and ammonia. The weight loss rates decrease above 600 °C due to P-N-O or P-N has characteristics of phosphorylated reagent, they make the polymer carbonization by the dehydration reaction [12].
Melamine phosphate powders absorb heat from the flame cooling combustible surface and generate non-combustible gases such as steam and ammonia diluting the oxygen of burning zone, and ammonia would accelerate the disappearance of free radicals OH· and H· to break off the combustion chain reaction. The inorganic cross-linked polymer (PNO)x covered on combustible surface to extinguish smoldering through oxygen-insulating. The carbonized layer formed by the dehydration reaction between P-N-O/P-N and wood crib would effectively prevent the wood crib return.

4. Conclusions

In this research we investigated the main physical properties of MP dry powders, the extinguishing properties of MP dry powders comparing with commercial ordinary ammonium phosphate powders and the thermal decomposition properties of melamine phosphate. Through the above researches, the conclusions are as follows.

The main physical properties of MP dry powders accord with the demands of Chinese Standards except the bulk density. The extinguishing properties of MP dry powders on Class A fires and Class B fires are higher than that of commercial ordinary ammonium phosphate powders.

The bulk density of MP dry powders was lower than the required value, the particles fall slowly, so the powders have better dispersion performance, and they can easily reach the burning surface through obstacles which is advantageous to extinguish fires especially smoldering.

The thermal decomposition properties of melamine phosphate explained the extinguishing mechanism of MP dry powders. The non-combustible gases such as steam and ammonia decomposed by melamine phosphate would cool combustible surface and dilute the oxygen of burning zone, ammonia would break off the combustion chain reaction through accelerating the disappearance of free radicals OH· and H·, The inorganic cross-linked polymer (PNO)x would cover on combustible surface to extinguish smoldering through oxygen-insulating.

References:


