Flame retardant properties of gas sealing materials used in coal mines

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Abstract: Flame retardants are key ingredients for gas sealing materials used in the coal mine wall. In this paper, the types and doses of flame retardants are investigated. The results showed that a gas sealing material with 11 wt % complex flame retardants had a good performance when the complex flame retardants were composed of aluminum hydroxide and chlorinated paraffin at a ratio of 3:8. The flame resistant property of this gas sealing material conforms to the safety standards of coal mines (MT113-1995). Furthermore, their mechanical properties met the standard requirements of the polymer cement waterproof coatings (GB/T23445-2009). The costs are very low compared with similar products in current practical use.

Keywords: flame retardant, coal mine, gas sealing materials, tensile strength, flame resistance properties.

Uniepalniacze w materiałach zabezpieczających ściany w kopalniach węgla przed wypływem gazu

Streszczenie: Zbadano wpływ rodzaju oraz ilości uniepalniacza, dodanego do emulsji styrenowo-akrylowej napełnionej krzemionką i cementem, na palność otrzymanej kompozycji zabezpieczającej ściany w kopalni węgla przed wypływem gazu. Efekt opóźnienia palenia na poziomie przewidzianym w normach bezpieczeństwa kopalń węgla (MT113-1995) uzyskano w wypadku zastosowania materiału uszczelniającego, modyfikowanego dodatkiem 11 % mas. kompozycji uniepalniacza, stanowiącej mieszaninę wodorotlenku glinu i chlorowanej parafiny w stosunku masowym 3:8. Modyfikowane materiały uszczelniające spełniają również wymagania pod względem właściwości mechanicznych, dotyczące polimerowo-cementowych powłok wodochronnych (GB/T23445-2009), a koszt ich wytwarzania jest dużo niższy niż koszt wytwarzania stosowanych obecnie produktów.

Słowa kluczowe: opóźniacz palenia, kopalnia węgla, materiały zabezpieczające przed wypływem gazu, wytrzymałość na rozciąganie, odporność na płomień.

Gas outbursts and explosions happen from time to time in the coal mining industry, which severely threatens the miners' safety and production of the coal mine [1, 2]. Gas sealing materials are required to prevent gas leaks from the coal mine walls [3]. Cement grouting materials are the traditional sealants due to their low cost and easy use. They do not easily cause fire or static electricity. However, water is used as a transmission medium and this water can leave cracks after material drying, which reduces the gas sealing efficiency [4, 5]. Polyurethane sealing materials are also frequently used to seal gas in coal mines. They can seal the cracks in the coal mine wall and prevent gas leakage. However, polyurethane is composed of inflammable organics, which limits its applications in underground coal mines [6, 7]. Another class of gas sealing materials are formed by combining polymer emulsions and cement. This can decrease the demand for water and cement. The some active groups of the polymer emulsion cross-linking reacted with the calcium and aluminum of cement or its hydration products. Then it formed a special bond bridge, which changed the internal structure and enhanced the compactness. So, polymer cement materials can prominently improve gas sealing performance [8–10]. However, polymer emulsions are flammable. Materials containing polymer emulsions do not meet the coal industry standard MT113-1995 [11]. Adding flame retardants to polymer emulsions are one effective solution to ensure the safety and efficiency of gas sealants in the coal mine [12].

Flame retardants have high heat capacities and low thermal conductivities so they can insulate heat and prevent temperature rises in the materials [13–15]. But if the selection of the flame retardant's type and dose are unsuitable, it will significantly deteriorate the physical-mechanical properties of the coal mine gas sealing material [16]. A balance between the flame resistance property and other properties of the materials are very important

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[17, 18]. In this paper, several typical flame retardants were investigated to determine the optimum flame retardant formulas for coal mine gas sealing materials.

EXPERIMENTAL PART

Materials

Styrene-acrylic emulsion S400F (Basf Company), quartz powder (Tianjin Guangfu Chemical Research Institute), portland cement (Taiyuan Cement Company), aluminum hydroxide (Tianjin Fuchen Chemical Reagent Company), ammonium polyphosphate (Tianjin Guangcheng Chemical Reagent Company), 70# chlorinated paraffin (Qingdao Yuzhou Chemical Company), magnesium hydroxide (Tianjin Guangfu Chemical Research Institute).

Experimental instruments

Fast paint dispersion experiment machine (Shanghai Environmental Engineering Technology Company, KS-370), analytical balance (Beijing Sados Instrument Company, BS214D), thermostatic drum wind drying oven (Shanghai Yuejin Medical Instrument Factory, 101-1-BS-II), sand grinding, dispersion, stirring installations (Shanghai Environment Engineering Technology Company, SFJ-400), multi-function tensile testing machine (Wenzhou Darong Textile Instrument Company, DR208).

Sample preparation

The styrene-acrylic emulsion and water were blended in the dispersion device for 1 min. The mixed solid powders (including quartz powder, portland cement and flame retardants) were poured in and stirred at a speed of 600 r/min for 5 min. Then, the mixture was left to rest for 3 min. Following, the blended mixtures were poured into the mold (150×150×3 mm) and the coating was formed. In order to easily de-mold, vaseline was applied to the mold surface before use. The coating was cured for 7 days under standard conditions (temperature: 23 ± 2 °C, relative humidity: 45–70 %). The thickness of the cured coating was 2 ± 0.2 mm [19].

Methods of testing

– GB/T176-96 method was adopted to test the ignition loss of ultra-fine fly ash.

– The surface drying time and full drying time of the coating were recorded in reference to the international standard GB/T16777-2008.

– After the coating was dried, the tensile strength of the material was determined by an electronic tensile tester (DL5000, Jianyi, Tianjin).

– American standard ASTM-D471 was used to evaluate the 7d water absorption of the material.

– SRT (stress-resistant technology) static electricity resistance was measured in accordance with the coal industry standard MT113-1995 with a surface resistance tester (EMI-20780, DESCO, USA).

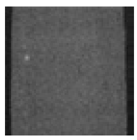
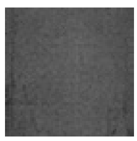
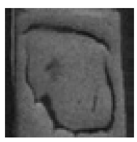
– The flame-retardant property of the material was assessed by an alcohol lamp and an alcohol blast burner with reference to GB/T7755-2003.

RESULTS AND DISCUSSION

Type selection of the flame retardants

Four typical flame retardants were selected to be compared in our experiments, including chlorinated paraf-

T a b l e 1. Type selection experiments of the flame retardants

Sample No.	Flame retardant/mass g	Portland cement g	Quartz powder g	Styrene acrylic emulsion g	Water cm^3	Apparent properties after mixing	Apparent properties after drying	Coating photos
1	Chlorinated paraffin/10	40	50	50	10	Normal	Smooth and elastic	
2	Ammonium polyphosphate/10	40	50	50	30	Viscous, release of ammonia	Cracked	
3	Aluminum hydroxide/10	40	50	50	10	Normal	Smooth and level	
4	Magnesium hydroxide/10	40	50	50	40	Very thick	Cracked and warped	

fin, ammonium polyphosphate, aluminum hydroxide and magnesium hydroxide. The dose of the flame retardants was set as 10 wt % of all powders and the ratio of styrene-acrylic emulsion to powders was set as 0.5. The apparent properties in the period of mixing and drying were tested and compared. The results are listed in Table 1.

It was observed that the coating of Sample 2 (ammonium polyphosphate) was sticky and cracked slightly. The reaction of ammonium polyphosphate with cement and its hydration products made the mixtures viscous, rapidly setting and difficult to coat. The coating of Sample 4 (magnesium hydroxide) was seriously cracked. The surface polarity of magnesium hydroxide is strong perhaps leading to its poor dispersion and compatibility, which made the mixtures clustered and unstable. After stirring for about 2 min, the material suddenly became very thick and it was not possible to stir or coat the material. Therefore, ammonium polyphosphate and magnesium hydroxide are unsuitable for gas sealing materials.

The coatings of Sample 1 (chlorinated paraffin) and Sample 3 (aluminum hydroxide) had good apparent properties, smooth and level. Their comprehensive properties were studied further in order to obtain the best formula of the flame retardants.

Influence of chlorinated paraffin dose on the properties of coatings

A series of coatings adding different percentages of chlorinated paraffin were prepared. The ratio of styrene-acrylic emulsion to powders was set as 0.5. Then, the mechanical and flame resistance properties were tested.

The tensile strength of the coating decreased and their elongation at break increased with higher chlorinated paraffin doses (Fig. 1). This is because chlorinated paraffin is not only a flame retardant but also a plasticizer. Chlorinated paraffin weakens the Van der Waals force between the emulsion molecules and reduces the strength of polymer molecule chains at the same time. So the elastic properties of the materials increased. According to the tensile property standard GB/T23445-2009 (tensile strength more than 1.8 MPa and elongation at break off more than 30 %), the appropriate dose of chlorinated paraffin was 2–17 wt %.

Figure 2 shows the influence of chlorinated paraffin dose on the material 7d water absorption ratio. With the increase of chlorinated paraffin dose, the 7d water absorption ratio of the material increased gradually. More chlorinated paraffin increased the viscosity of the coating and the many bubbles formed by stirring were difficult to eliminate. These bubbles within the coating surface increased the surface area and increased the water absorption as well. In order to make the 7d water absorption ratio less than 6 %, the dose of chlorinated paraffin was less than 10 wt %.

The heated chlorinated paraffin could release hydrogen chloride gas. Its specific gravity is greater than air so

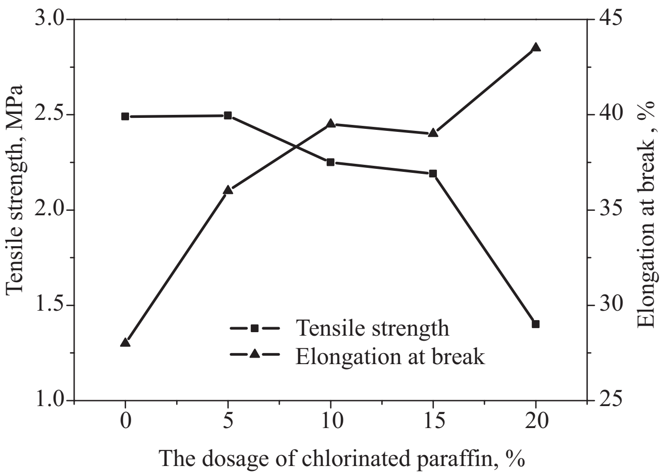


Fig. 1. Influence of chlorinated paraffin dose on the tensile property of coatings

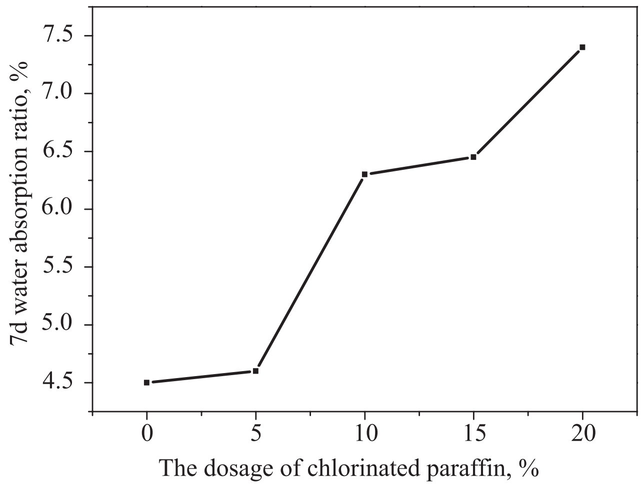


Fig. 2. Influence of chlorinated paraffin dose on the 7d water absorption ratio of coatings

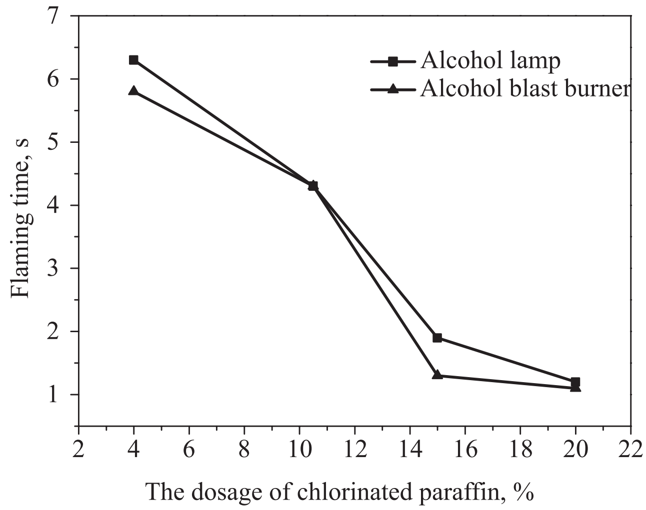


Fig. 3. Influence of chlorinated paraffin dose on the flame retardant property of coatings

it could deposit on the surface of combustible materials, and then form a flame retardant covering. And the flaming time of materials was shortened significantly with the increase of chlorinated paraffin dose (Fig. 3). When the dose of chlorinated paraffin was more than 12 wt %, the flame retardant effect meets the standard requirements of MT113-1995. Adding more chlorinated paraffin will increase the cost and toxic smoke volume. Taking the tensile properties and flaming resistance property into account, the appropriate dose of chlorinated paraffin is about 10–12 wt %.

Influence of aluminum hydroxide dose on the coating properties

A series of coatings with different percentages of aluminum hydroxide were prepared. The ratio of styrene-acrylic emulsion to powders was set as 0.5. Then, the mechanical and flame resistance properties were tested.

Aluminum hydroxide can react with cement and its hydration products, which would promote the cement hydration reaction and fill the spaces in cement. With the increase of aluminum hydroxide dose, the coating was more compact and non-elastic. So, the tensile strength of the coatings increased and their breaking elongation decreased gradually, shown in Fig. 4. The tensile strength of all the tested samples was greater than 1.8 MPa, meeting the standard of GB/T23445-2009. In order to make the breaking elongation more than 30 %, the aluminum hydroxide dose must be kept less than 12 wt % of the whole powders.

It is suggested that the pore structure was the main factor for water absorption (see earlier text). Aluminum hydroxide reacted with the cement and its hydration products. More aluminum hydroxide made the structure of the coating more compact, that is, less porous in the coating. So, the 7d water absorption ratio of the materials decreased with greater aluminum hydroxide doses (Fig. 5). The data were all in the range of 4.0–5.5 wt %, which all agreed with the standard (less than 6 wt %).

The flaming time of the material shortened significantly with higher aluminum hydroxide doses (Fig. 6). When the coating was burned, aluminum hydroxide can be decomposed at 200 °C and this process can absorb a lot of heat. Thus, the temperature of the polymer coating decreased and the flame rate slowed down. The water of decomposition could dilute the combustible gas and oxygen concentration. The difficult-flammable aluminum oxide decomposed by aluminum hydroxide deposited in the polymer surface. They played a good role in flame resistance for polymer [20]. It can be seen from Fig. 6 that if aluminum hydroxide was used as the only flame retardant, its dose needs to be more than 20 wt % to meet the standard of MT113-1995. However, adding more aluminum hydroxide would increase the cost, produce more toxic smoke, and reduce several beneficial properties of the material such as breaking elongation and elasticity. Therefore, aluminum hydroxide cannot be used as the

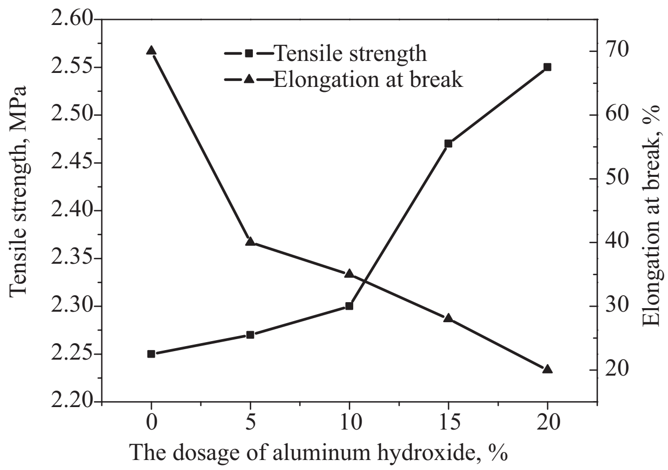


Fig. 4. Influence of aluminum hydroxide dose on the tensile property of coatings

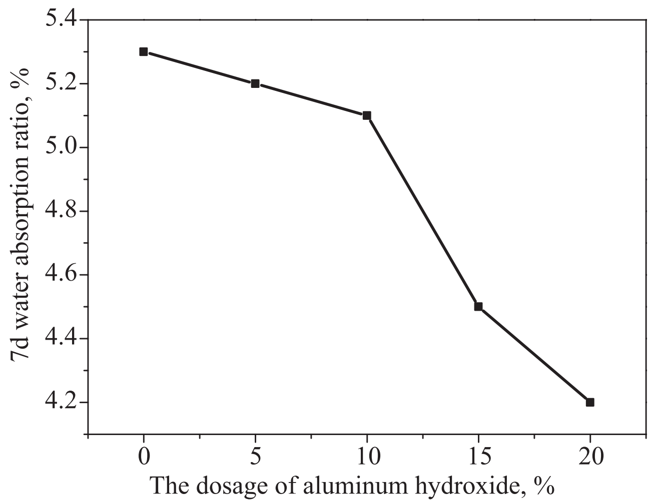


Fig. 5. Influence of aluminum hydroxide dose on the 7d water absorption ratio of coatings

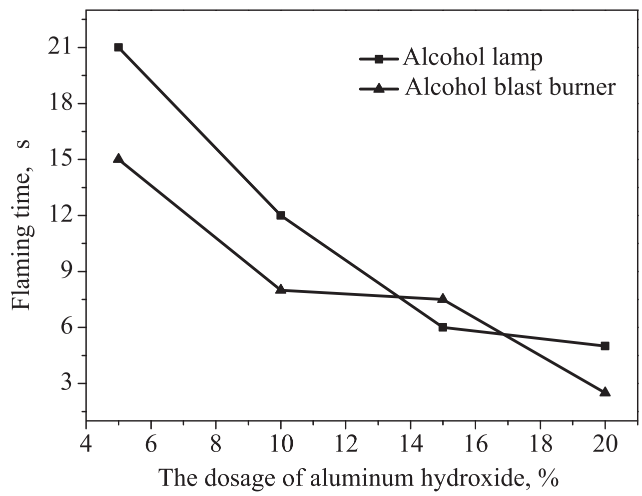


Fig. 6. Influence of aluminum hydroxide dose on the flame retardant property of coatings

main flame retardant, only as an auxiliary flame retardant and smoke suppressant. In order to increase the comprehensive properties and to reduce the cost, complex flame retardants were investigated further.

Influence of complex flame retardants on the resistance property of coatings

Two complex flame retardants formulas were prepared: 10 wt % chlorinated paraffin and 5 wt % aluminum hydroxide (Sample 5), 8 wt % chlorinated paraffin and 3 wt % aluminum hydroxide (Sample 6). The ratio of styrene-acrylic emulsion to powders was set at 0.5. The results of the flame experiment are shown in Table 2.

The flame resistance effects of the complex flame retardant formulas were better than that of simple samples. This is because the chlorinated paraffin has a good flame retardant property but it will promote the polymer materials released smoke in the fire; for aluminum hydroxide, its smoke suppression effect was good but it reduced the mechanical properties of the material significantly. However, complex flame retardants could be used in reduced doses and produce less smoke, as well as make materials with lower halogen content. The complex flame retardants composed of chlorinated paraffin and aluminum hydroxide with a mass ratio of 8:3 had better flame resistance properties. Thus could guarantee the material mechanical performance changed little, and improve efficiently the flame resistance property by the synergistic effect. So the dose of flame retardants was reduced and the cost was also less.

The comprehensive properties of the gas sealing material

The samples were prepared in accordance with the best formula obtained above. Their comprehensive properties were tested by the national production safety inspection center of Taiyuan Mining Equipment and the Academy of Building Research of Shanxi. The results are listed in Table 3, and the properties met the requirement of ES. CHN. Q/140402LA 003-2015.

T a b l e 2. Flaming time and smoke time of different flame retardant formulas

The test items		Standard of MT113-1995	Sample 5 10 wt % chlorinated paraffin + 5 wt % aluminum hydroxide	Sample 6 8 wt % chlorinated paraffin + 3 wt % aluminum hydroxide
Alcohol blast burner	Flaming time/s	Less than 3 s	1.2	1.3
	Smoke time/s	Less than 10 s	8	8
Alcohol lamp	Flaming time/s	Less than 6 s	2.2	2.5
	Smoke time/s	Less than 20 s	13	15
Met the standard			Yes	Yes

Jie trafigura is a type of sealing materials with good flexibility. It is usually sprayed on the wall of coal mines. It can prevent air leakage and gas emission to a certain extent. Compared with Jie trafigura (Haoke Weibo Mining Engineering Company Co., Ltd), the comprehensive properties of the sealing material developed in this paper were better. The standard of the tensile strength and static electricity resistance were especially much better.

CONCLUSIONS

The flame retardant formulas used in coal mine gas

T a b l e 3 Comprehensive properties of the coatings

Item			Q/140402LA 003-2015	Sample in this paper	Jie trafigura
Surface drying time, h			≤ 4	2	
Full drying time, h			≤ 48	8	
Tensile strength, MPa			≥ 2.0	2.2	1.2
Breaking elongation, %			≥ 30	52	56
Inherent tensile strength, MPa			≥ 20	2.0	
Flame retardation	Alcohol blast burner test	Combustion time with flame, s	≤ 3	1.1	Fire rating: flame retardant materials
		Combustion time without flame, s	≤ 10	8.4	
		Length of flame extension, mm	≤ 280	95~109	
	Alcohol lamp test	Combustion time with flame, s	≤ 6	2.2	
		Combustion time without flame, s	≤ 20	11.4	
		Length of flame extension, mm	≤ 250	80~89	
Static electricity resistance, Ω			≤ 3×10^8	0.45×10^5	≤ 10^9
Water tightness (0.3 MPa, 30 min)			Impermeable	Impermeable	

sealing materials were investigated. Taking the apparent properties of the coating as the inspection target, aluminum hydroxide and chlorinated paraffin suited the flame retardants. Taking the mechanical properties into account, aluminum hydroxide and chlorinated paraffin were not added more to than 10 wt % and 12 wt %, respectively, as simple additives. Hoewver, under such conditions, their flame resistance properties could not meet the standards. Then, complex flame retardants formulas were obtained composed of aluminum hydroxide and chlorinated paraffin at a ratio of 3:8. Their flame retardant properties meet the requirement of MT113-1995 standard.

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