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Research on the Temperature Control of Emulsion Explosive's Rapid Reaction by Chemical Blasting

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Abstract

The porous granular ammonium explosive is a mixture of porous granular ammonium nitrate and oil (diesel, etc.) as the main components of an explosive mixture without sensitizer. It has the advantages of low cost, easy manufacture, good safety, convenient use, etc. advantage. In order to understand the effect of compound emulsifier on the thermal stability of heavy ammonium explosives, a C80 microcalorimeter was used to analyse the thermal decomposition characteristics of heavy ammonium explosives prepared from single emulsifier and compound emulsifier at a constant heating rate of 1K/min. Calculate the kinetic and thermodynamic parameters in this process. The results showed that the addition of the compound emulsifier inhibited the thermal decomposition of the heavy ammonium explosive, and increased the reaction starting temperature and the peak temperature of the heavy ammonium explosive. At the same time, the increase in activation energy indicates that the heat stability and thermal safety of heavy ammonium explosives prepared by using composite emulsifiers are higher than that of using single emulsifiers.

Keywords

Ammonium Explosive; Thermal Stability; Compound Emulsifier; Thermodynamics; Temperature Control.

1. Introduction

Heavy Ammonium Explosive (HANFO) is made by adding a certain proportion of latex matrix on the basis of Ammonium Explosive. During the mixing process, the high-density latex matrix is filled between the pores of the porous granular Ammonium Explosive and attached to the ammonium nitrate particles. On the surface, the density, detonation energy, detonation speed and water resistance of heavy ammonium explosives are greatly improved [1]. In addition, it has outstanding advantages such as low price, wide source of raw materials, high safety, and flexible ratio. The C80 microcalorimeter has been widely used in thermal analysis.

Its basic principle is similar to DSC, but it has higher sensitivity and the ability to measure gram-level liquid or solid matter. Therefore, a constant heating rate of 1K/min is used to study the thermal behaviour of a single emulsifier and a composite emulsifier to prepare heavy ammonium explosives, and calculate the thermodynamic and kinetic parameters in this process to evaluate its safety [2]. The objective understanding of thermal safety also provides a new direction for how to improve the thermal safety of heavy ammonium explosives.

2. Experimental Design

2.1. Explosive raw materials and formula

The raw materials include: porous granular ammonium nitrate, light diesel oil (0#), ammonium nitrate, sodium nitrate, water, Inner Mongolia wax, emulsifier A (Span-80), emulsifier B (T-152). The formula of the latex matrix is shown in Table 1, and the formula of the heavy ammonium oil explosive is shown in Table 2.

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Table 1. Raw materials and formula of latex base (%)

Latex base material	1#	2#	5#	4#	5#
Ammonium Nitrate	75	75	75	75	75
Sodium Nitrate	8	8	8	8	8
water	10.5	10.5	10.5	10.5	10.5
Inner Mongolia Wax	4	4	4	4	4
Emulsifier A	2.5	1.67	1.25	0.83	0
Emulsifier B	0	0.83	1.25	1.67	2.5

Table 2. The raw materials and formula of heavy ammonium explosives

Heavy Ammonium Explosive Material	w/%
Porous granular ammonium nitrate	80.33
Diesel (0#)	4.67
Latex matrix	15

It can be seen from Table 2 that as the content of the latex matrix increases, the explosion heat and temperature values of the heavy ammonium explosives show a downward trend. This is because: (1) The water in the latex matrix has a high heat capacity, which is During the process, a phase change occurred, which caused the water to absorb part of the heat of the system in the explosive reaction of the explosive, thereby reducing the explosive heat value of the explosive; (2) The H/C content ratio of porous granular ammonium explosives was significantly higher than that of emulsion explosives. The higher the H/C content ratio in explosives, the greater the explosion heat value. Therefore, as the content of the latex matrix increases, the explosion heat and temperature values of heavy ammonium explosives show a downward trend.

2.2. Theoretical calculation basis for explosive thermochemical parameters

2.2.1. Determination of the explosive reaction equation of explosives

The calculation of the thermochemical parameters of explosives needs to determine the explosive reaction equation. In this paper, the classical B-W method is used to establish the explosive reaction equation of the modified ammonium explosive.

2.2.2. Calculation of explosive heat

Combining the explosive reaction equation and according to Gas's law, the constant volume heat generation data of the explosive components and explosive products at 298K are used to calculate the constant volume detonation heat of the explosive:

$$Q_V = Q_{V1.3} - Q_{V1.2} \tag{1}$$

Q_V is the constant volume explosive heat of the explosive. $Q_{V1.3}$ is the sum of the heat generated by the constant volume of the explosive product. $Q_{V1.2}$ is the sum of the constant volume heat generation of each component of the explosive, and the unit is $kJ g kg^{-1}$.

2.2.3. Calculation of explosive temperature

Detonation temperature refers to the highest temperature that the explosive product is heated to by the energy released at the moment of explosion, and it is one of the important performance indicators of explosives [3]. Using the calculation results of the constant volume explosion heat and the average constant volume heat capacity of the explosion product C=A+Bt, the maximum temperature that the explosion product can reach is calculated, which is the theoretical explosion temperature. The calculation formula of explosion temperature is as follows, where T_0 is 298K:

$$t = -A + \frac{\sqrt{A^2+4BQ_V\times1000}}{2B} \tag{2}$$

$$T_b = t + T_0 \tag{3}$$

$$A = \Sigma n_i a_i, B = \Sigma n_i b_i \tag{4}$$

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In the formula, n_i represents the number of substances in the i explosive product, in mol; a_i, b_i represents the coefficient of the average constant volume heat capacity $\bar{C}_{V,i} = a_i + b_i t$ of the i explosive product. The unit of $\bar{C}_{V,i}$ is $J gmol^{-1\circ}C^{-1}$. T represents the temperature interval, in °C. The absolute value of Q_V is taken when it is brought into the calculation.

2.3. Experimental equipment and procedures

This experiment uses a C80 microcalorimeter, and its unique CS32 controller is connected to a computer to record the experimental data [4]. The calorimeter is equipped with a 3D Calvet sensor, which can completely surround the sample to ensure the accuracy of heat measurement and create a stable heating environment. The relevant technical parameters are: sample mass: 0-10g; sensitivity is about 10-6! W; measurable temperature range: room temperature to 573K; program temperature scan rate: 0.01-2K/min. The experimental atmosphere is air, and the reference substance is α-Al_2O_3. In order to observe the extremely small heat flow changes during the heating process, heating is performed at a constant rate of 1K/min from room temperature to 300°C, and the cooling stage is set to 2K/min. The structure of the C80 device is shown in Figure 1.

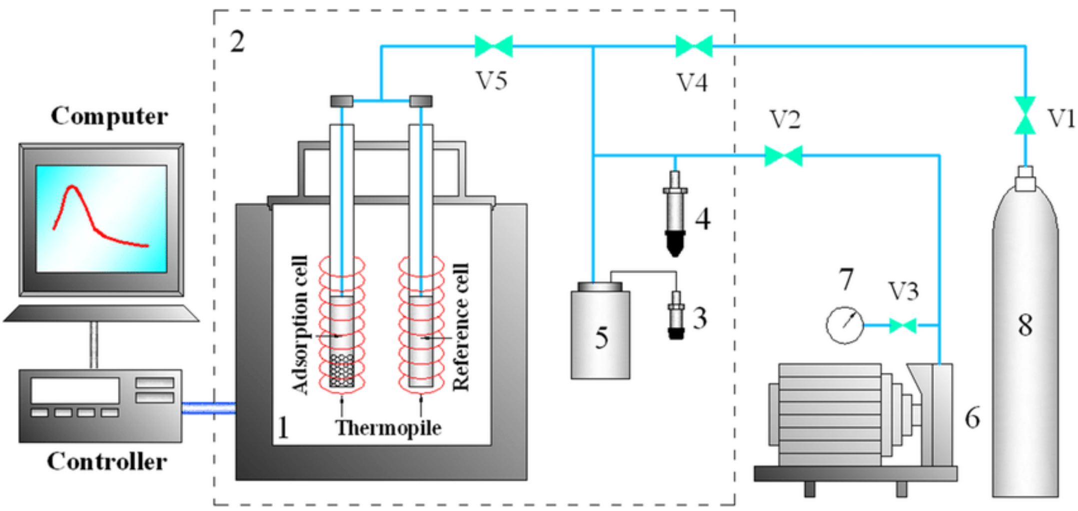

Figure 1. Microcalorimeter C80 test system

3. Experimental results

3.1. Calculation results of explosive heat

The constant volume detonation heat calculation results of the explosive at 298K are shown in Table 3. The explosion heat in Table 3 is the heat actually used to raise the temperature of the explosion product after deducting the phase change heat Q (H_2O) of water. It can be seen from Table 3 that the explosive heat of the porous granular ammonium explosive is the highest, and the explosive heat of the emulsion explosive is the lowest; as the content of the latex matrix increases, the explosive heat value of the explosive gradually decreases.

Table 3. Explosive heat calculation results

Parameter		Hot QV
Porous Granular Ammonium Explosive		3844.28
	25: 75	3707.53
m (emulsion explosive): m (porous granular ammonium explosive)	50: 50	3288.39
	75: 25	3427.28
Emulsion explosive		3288.39

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3.2. Thermal decomposition characteristics of explosives

Figure 2 shows the C80 curve of 1#~5# explosive samples at a heating rate of 0.2℃•min^{-1}.

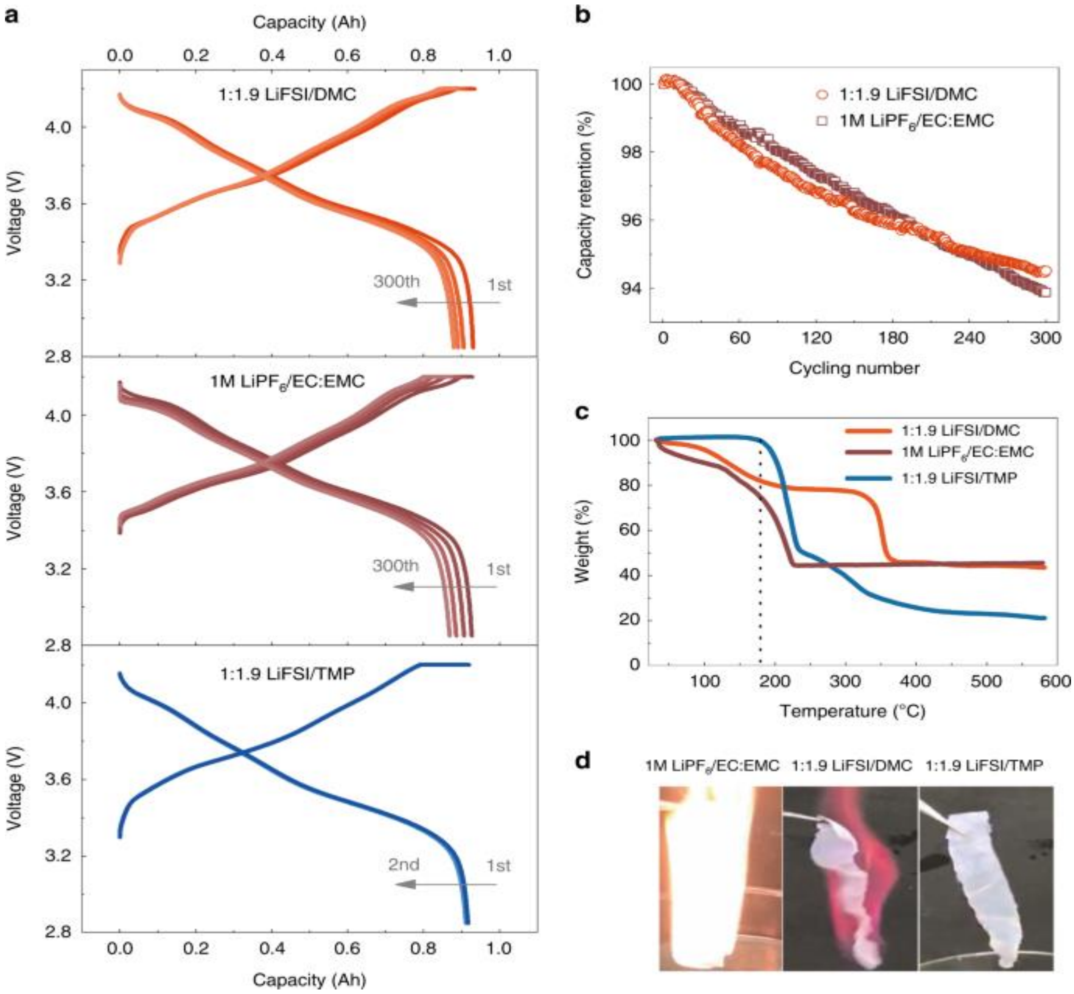

Figure 2. Heat flow curve of sample 1#~5# in air atmosphere

It can be seen from Fig. 2 that there are endothermic peaks in the range of 39~130℃ for 5 kinds of explosive samples of 1#~5#, which is caused by the crystal form transformation of solid ammonium nitrate. Compared with sample 1#, the test the number and peak size of the endothermic peaks of sample 2# and 5# are significantly reduced, indicating that the addition of emulsion explosives has an inhibitory effect on the crystallization of solid ammonium nitrate [5]. According to the analysis, it is believed that the emulsion explosive covers the surface of the porous granular ammonium explosive, which conceals the endothermic phenomenon of the porous granular ammonium explosive at this stage. The third endothermic peak of sample 1# is obviously broadened, which may be in the emulsion explosive. The result of the combined effect of the endothermic heat of evaporation of water and the released water after the demulsification of the latex particles and the crystal transformation of the solid ammonium nitrate particles.

The starting temperature of the thermal decomposition reaction of heavy ammonium oil explosive samples 1#~5# are: 197.17℃, 205.91℃, 216.25℃, 222.51℃, and 202.0℃. It can be seen that with the addition of emulsifier B (T-152), the starting temperature of the heat released by the thermal decomposition of heavy ammonium explosives increased first and then decreased. The starting temperature of thermal decomposition of sample 4# heavy ammonium explosives maximum. The starting temperature of the exothermic reaction is not only an

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important parameter to measure the degree of difficulty of the chemical reaction of the explosive, but also an important index to measure the thermal risk of the explosive. It is generally believed that the higher the starting temperature of the exothermic reaction, the more difficult the explosive decomposition and the more stable the explosive will be. Therefore, it is considered that the stability of sample 4# is higher than that of the other 4 groups of samples. Analysis shows that when w emulsifier A: w emulsifier B is 1:2, the composite emulsifier has an excellent matching effect with the oil phase material, and can densely fill the gaps of porous ammonium nitrate particles and uniformly cover the surface of the ammonium nitrate particles, thereby This increases the stability of heavy ammonium explosives.

3.3. Discussion on the influence of explosive thermochemical parameters

The explosive heat and temperature values of porous granular ammonium explosives are the largest, and the explosive heat and temperature values of emulsion explosives are the smallest; with the increase of the latex matrix content, the explosive heat and temperature values of heavy ammonium explosives show a decreasing trend. This is because: 1) The water in the latex matrix has a high heat capacity. During the explosion process, the phase change of the water causes the explosive to absorb part of the heat of the system during the explosion reaction, thereby reducing the explosive heat value of the explosive; 2) The n(H)/n(C) of heavy ammonium explosives is significantly higher than that of emulsion explosives. Obviously, explosives with high n(H)/n(C) have a larger explosion heat. Therefore, with the content of latex matrix the explosive heat value of heavy ammonium explosives shows a downward trend.

The data is processed through Origin software, as shown in Figure 3. It can be seen from Figure 3 that the effect of the mass fraction of the latex matrix on its explosion heat and temperature is approximately linear. Therefore, through Figure 3, the approximate value of the explosion heat and explosion temperature corresponding to any mass fraction of the latex matrix can be found; the mass fraction of the latex matrix The impact on explosion heat is more obvious than the impact on explosion temperature.

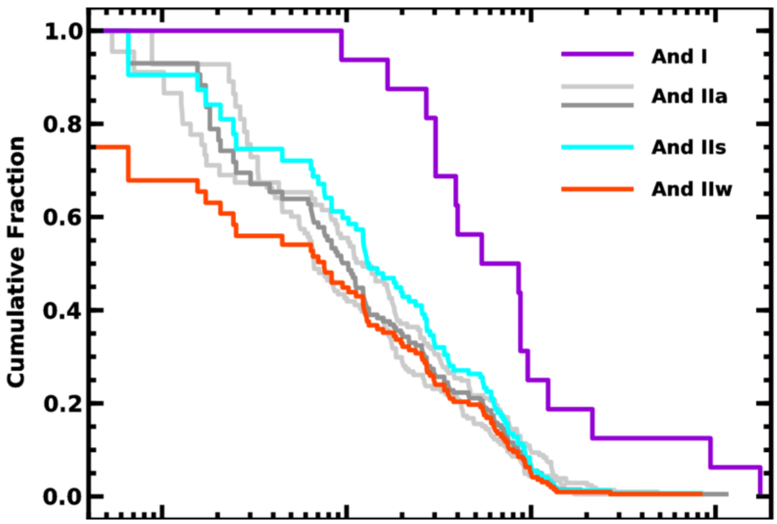

Figure 3. Relationship curve between latex matrix mass fraction and thermochemical parameters

4. Conclusion

The explosive heat and temperature of heavy ammonium oil explosives showed a downward trend with the increase of the content of the latex matrix. The reason for the endothermic peak of the C80 curve of heavy ammonium explosives is the crystal transformation of some solid ammonium nitrate particles, and the emulsion explosives inhibited the endothermic

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phenomenon of porous granular ammonium explosives. The thermal stability of heavy ammonium explosives is higher than that of emulsion explosives.

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