Safety Study of the Chlorate Firecrackers

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Abstract: The traditional firecrackers composition is mainly composed of potassium chlorate, sulfur and aluminum powder. Its thermal safety, friction and impact sensitivity were studied in this paper. Thermal safety was tested by Accelerating Rate Calorimeter (ARC). Test results showed that the thermal stability of chlorate composition was lowest among the nitrate composition and perchlorate composition. While the impact sensitivity of chlorate composition was 16% higher than that of nitrate composition, 76% higher than that of perchlorate composition; the friction sensitivity of chlorate composition was 5% higher than that of nitrate composition, 45% higher than that of perchlorate composition.

Keywords: accelerating rate calorimeter; solid state reaction; thermal safety; mechanical sensitivity

1 Introduction

Fireworks Firecrackers consist of oxidant, reducer and adhesive, etc [1]. Any heat, mechanical stimulation, chemical energy and other human error can cause the pyrotechnics combustion, and even explosion. Referring to the published statistic data of the detonating agent & pyrotechnics, the thermal explosion counts 12% of total accidents of the pyrotechnics, due to the heating or heat accumulation inside the material; while, impact and friction both count 72% of the all accidents[2]. Therefore, it is very necessary to study the safety of fireworks firecrackers. This paper focuses on the thermal safety and mechanical sensitivity of the chlorate firecrackers.

2 Thermal Safety of Chlorate Firecrackers

2.1 Thermal Safety Experiments

2.1.1 Brief introduction of experimental apparatus

The apparatus is accelerating rate calorimeter (ARC) made by Columbia Scientific Industries of Austin, Texas USA under an abbreviated name CSI-ARC [3-4].

2.1.2 Samples and test conditions

The samples all adopt zero oxygen balance prescription; Table 1 shows the type of samples and the test conditions as well.

Table 1 Type of samples and the test conditions

sample name	sample number	sample mass/g	bomb mass/g	start temperature/℃	Slopesensitivity /(℃·min^{-1})
$KClO_3$ 70%, Al 20%, S 10%	1	0.1574	21.6162	50	0.02
KNO_3 70%, Al 20%, S10%	2	0.5034	21.6162	200	0.02
$KClO_4$67%, Al 20%, S13%	3	0.5006	21.4360	200	0.02

2.2 Results and Discussion

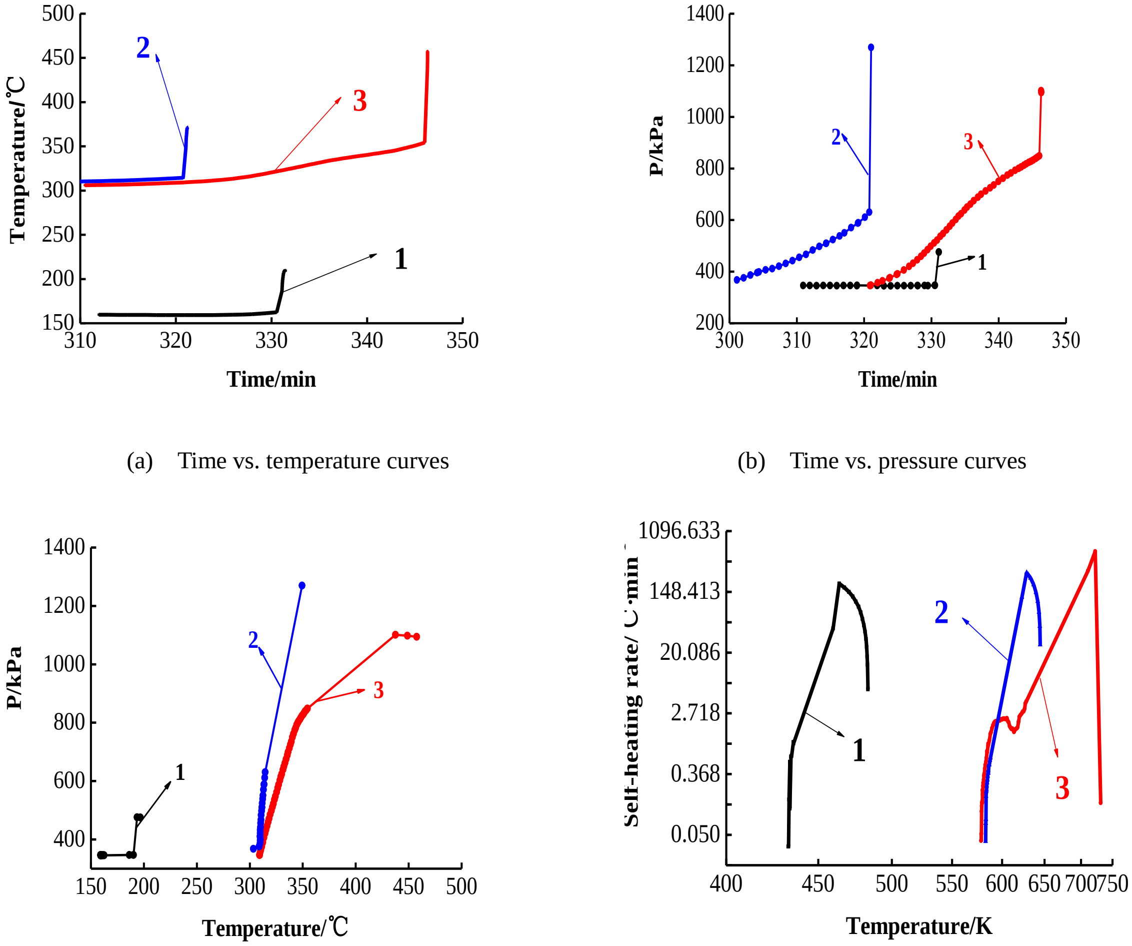
Curves of test samples are given in Fig.1.

We can see from Fig.1(a) that the onset exothermic temperature of sample No.1 is lowest among the three kinds of pyrotechnics which is only 159.26 ℃, while the other two pyrotechnics are all around 300 ℃. At the same time, when the apparatus detects the exothermic reaction, the temperature of three samples all rise rapidly. Fig.1(b) shows the pressure of three samples all reach the maximum in short time. Moreover, for the sample No.2 and sample No. 3 pyrotechnics, it can be seen that the pressure of nitrate composition increases much more than that of perchlorate composition.

In Fig.1(c), it is showed that the temperature and pressure for all three samples increase simultaneously when the exothermic reaction takes place, so the explosion risk is high. The pressure of sample No.1 jumped abruptly at 159.26 ℃, while the sample No.2 and sample No.3 are 294.79 ℃ and 309.50 ℃ respectively. Fig.1 (d) shows that the maximum temperature rise rate of sample No.1 is highest among the three samples, which has least sample mass. While the temperature rise rate of sample No.2 is larger than sample No.3 with the same mass, due to the decomposition heat of nitrate (-3.14 kJ·g^{-1}) is higher than perchlorate (-0.04 kJ·g^{-1}).Combine the Fig. (a),(b) with (d), it can be found that the time to maximum temperature rise rate of sample No.1 is 6.17 min , while the sample No.2 and sample No.3 are 14.71 min and 46.85 min respectively.

Form the analysis of the experiments data, it can be seen that the thermal satiability of chlorate firecrackers is worst among the three samples, which is due to the lowest ignition temperature of the chlorate composition. So the thermal hazard of chlorate firecrackers is highest. The phenomenon can be explained by the Solid Chemistry. The three pyrotechnics reaction systems belong to the solid state reaction. From the view of the solid chemistry, the fundamentality of solid state reaction is that the reaction temperature of the system decreases, which is caused by the "crystal lattice rattle" and crystal diffusion of oxidants. The "crystal lattices rattle" and crystal diffusion are dominated by the factors of thermodynamics and dynamics. They cause the Preignition Reaction (PIR) of the pyrotechnic system. The "crystal lattice rattle" is measured by Tammann temperature. Table2 shows the

Tammann temperature of three oxidants [5]:



(a) Time vs. temperature curves (b) Time vs. pressure curves

(c) Temperature vs. pressure curves (d) Temperature vs. self-heating rate curves

(1 - chlorate composition, 2 - nitrate composition, 3 - perchlorate composition)

Fig.1 Adiabatic decomposition curves of sample No.1-3

Table2 Tammann temperature of three oxidants

oxidants	melting point /K	Tammann temperature /℃
$KClO_3$	629	42
KNO_3	607	31
$KClO_4$	883	168

It can be seen from Table 2, the Tammann temperature of chlorate is 42 ℃. Although the Tammann temperature of nitrate is lower, the bond length of Cl-O (0.157 nm) is longer than that of N-O (0.136 nm), and bond energy of Cl-O (244 $kJ \cdot mol^{-1}$) is lower than that of N-O (305 $kJ \cdot mol^{-1}$), so much more energy will be used to break the chemical bonds in the N-O; it may increase the reaction energy. Because the Tammann temperature of chlorate is lower, when the chlorate connects with the low melting point reducer such as sulfur and other easily flowing liquid, the system has higher reaction ability. It is because that these low melting point reducers can infiltrate into crystal lattice of chlorate easily. In conclusion, chlorate can cause reaction much easier than nitrate.and perchlorate

2.3 Determination of Kinetic Parameters

The method of pseudo-inverse matrix method is used to calculate the kinetics parameters [6]. The activation energy and pre-exponential can be calculated by using the correlation software. Table 3 shows the results.

Table3 Kinetic parameters of pyrotechnics

sample number	1	2	3
Ea/ ($kJ \cdot mol^{-1}$)	322.9	437	408
A /min^{-1}	3.26×10^{32}	7.3×10^{42}	2.8×10^{40}

3 Mechanical Sensitivity of Chlorate Firecrackers

3.1 Friction Sensitivity Experiments

Friction sensitivity test is measured by pendulum-type friction apparatus, pendulum angle is 80°,pressure is 2.5MPa, hammer mass is 1.5kg, each group has 25 individuals, the mass of each test sample is 20mg.Table 4 shows the results.

Table4 Friction sensitivity test results of three samples

sample name	sample number	explosion probability/%
chlorate firecrackers	1	90
nitrate firecrackers	2	85
perchlorate firecrackers	3	45

3.2 Impact Sensitivity Experiments

Impact sensitivity test adopt WL-1-type drop hammer apparatus, hammer mass is 10kg, drop high is 250mm, each group has 25 individuals, the mass of each test sample is 40mg. Table 5 shows the results.

Table5 Impact sensitivity test results of three samples

sample name	sample number	explosion probability/%
chlorate firecrackers	1	96
nitrate firecrackers	2	80
perchlorate firecrackers	3	20

From Table 4 and Table 5, it can be seen that the friction sensitivity of chlorate composition is 5% higher than that of nitrate composition, 45% higher than that of perchlorate composition; the impact sensitivity of chlorate composition is 16% higher than that of nitrate composition, 76% higher than that of perchlorate composition.

4 Conclusions

We can draw the following conclusions through the analysis results of chlorate firecrackers, nitrate firecrackers and perchlorate firecrackers.

(1) Compared with nitrate firecrackers and perchlorate firecrackers, the thermal safety of chlorate firecrackers is worst. Its onset exothermic temperature is lowest(159.26 ℃); while the time to the maximum temperature rise rate is only 6.17 min, so the risk of thermal explosion is highest. On basis of above, during manufacture, storage and transportation of chlorate firecrackers, strictly environmental conditions and safety operation regulation are needed.

(2) The mechanical sensitivity of chlorate firecrackers is high; the impact sensitivity of chlorate composition is 16% higher than that of nitrate composition, 76% higher than that of perchlorate composition. The friction sensitivity of chlorate firecrackers is 5% higher than that of nitrate composition, 45% higher than that of perchlorate composition.

(3) Owing to the high sensitivity of chlorate firecrackers, it has strict regulation on the chlorate use in home and abroad. However, up to now, chlorate is still the best low ignition point oxidant in the pyrotechnics, compared with nitrate and perchlorate. To be safety, therefore, we can take more measures to decrease the risk of chlorate based on the above experiment results. For instance, we can change the characteristics of chlorate by nanotechnology, or screen reducer which has good compatibility with chlorate etc. All that can obviously decrease the occurrence of accidents during manufacture, storage and transportation of firecrackers, which also have notable economy benefit and social benefit as well.

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