Research paper

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Comparative study of the combustion characteristics for modified barium nitrate and ordinary barium nitrate

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Abstract

To meet the urgent demand of civil firework industry for safe oxidants, based on the preparation of the modified barium nitrate (Ba(NO₃)₂), the combustion characteristics of the modified Ba(NO₃)₂/Mg were studied experimentally. The results revealed that the modified Ba(NO₃)₂lowers the flame temperature and increases luminous intensity for Ba(NO₃)₂/Mg system that reacted in air. To explain this phenomenon, we suggest that the presence of metal oxides (NiO, CoO and Cu₂O) and the other productions in the modified Ba(NO₃)₂, which will absorb some heat energy when the modified Ba(NO₃)₂/Mg system reacts, thereby lowering the flame temperature. The other explanation is that the presence of metal oxides, when it is heated up, will increase the luminous intensity of the reaction system.

Keywords : pyrotechnic mixtures, combustion, luminous intensity, barium nitrate

1. Introduction

Pyrotechnics are used in a variety of military and civil applications. One such application is coloured signal flares¹⁾⁻⁵⁾. Many such pyrotechnic flare compositions contain barium nitrate, which acts as the oxidizer⁶⁾, and the use of barium nitrate in light-producing compositions has been investigated^{7),8)}. However, compared to explosive potassium perchlorate, barium nitrate has the defect that they are difficult to ignite and its flame is easy to die out due to its higher melting point and heat absorption when it undergoes decomposition, so the modified barium nitrate was prepared by Chen et al.⁹⁾ and Z. Babar¹⁰⁾, and then its physical and chemical properties were tested. However, to the best of our knowledge, the comparison study of the modified barium nitrate and ordinary barium nitrate has not been performed.

Pyrotechnic formulations containing magnesium and barium nitrate are used in pyrotechnic illuminating compositions, and they have been studied¹¹⁾, as well as the

binder systems and their influence on the combustion characteristics of the formulations ^{12),13)}. In this research, we have started the work towards understanding the combustion characteristics of the pyrotechnic mixtures of modified barium nitrate and ordinary barium nitrate with magnesium. Results of this work should provide valuable information for selecting oxidizer to be used in manufacturing pyrotechnics.

2. Experimental 2.1 Materials

The materials used were barium nitrate (Ba(NO₃)₂, > 98% pure, 90 mesh (165 μ m)) purchased from Anqiu Hongru Chemical Company (Anqiu, Shandong, China); nickel oxide (NiO, chemically pure, 120 mesh (124 μ m)) purchased from Henan Huayu chemical raw materials Company Ltd. (Zhengzhou, Henan, China). And then some of the Ba(NO₃)₂ were modified. The modified method and process were described previously by Chen et al.⁹.

Table 1Composition of samples and weight [wt.%].

No.	Modified Ba(NO3)2	Ordinary Ba(NO3)2	Mg	PR	NiO
1	72.7	_	24.3	3	_
2	—	72.7	24.3	3	_
3	-	70.2	21.8	3	5

Magnesium (Mg, >98% pure, 120 mesh $(124 \mu m)$) purchased from Northeast Light Alloy Company Ltd. (Harbin, Heilong-jiang, China), phenolic resin (PR, >96% pure, 90 mesh (165 μ m)) purchased from Shandong Shengquan Chemical Company Ltd. (Zhangqiu, Shandong, China).

2.2 Methods

2.2.1 Preparation of samples

The pyrotechnic mixtures, containing modified Ba $(NO_3)_2/Mg$, ordinary Ba $(NO_3)_2/Mg$, and ordinary Ba $(NO_3)_2/Mg/NiO$ are shown in Table 1 with their weight ratios.

The dry chemicals required to prepare 60 g batches of the formulations in Table 1 were weighed out and dried in an oven overnight at 50°C. The chemicals were then individually sieved through a 90 mesh (165μ m) screen. The sifted chemicals were then mixed with adhesive (phenolic resin which was dissolved in acetone before being mixed) and blended by hand until homogeneity was achieved. After mixing, the formulations were passed through a 40 mesh (373μ m) sieve. The granules were dried in air for 2-3 h at ambient temperature to ensure partial curing before consolidation. The mixtures were weighed out in five 10 g portions and pressed into pellets by using a 25-ton-pressure oil pressure machinery under 3 MPa with a dwell time of 5s, the average height of the pellets are shown in Table 2.

Five pellets of each formulation were pressed and initiated with an electric match at a voltage of 5 V.

2.2.2 Combustion characteristics

The experiments were performed in a laboratory photometric chamber (darkroom). The burning flame temperature of each pellet was measured by IGA-140 noncontact far-infrared thermometer (IMPAC). In addition, at the same time, the burning luminous intensity of each pellet was measured by a transient intensity testing instrument (Xi'an Institute of Applied Optics). The burn rate of each pellet was measured by target lines at constant pressure (it is a test method of measuring the burning rate of pyrotechnics, and first applied to test the burning rate of the solid propellant. For the test procedure, see reference¹⁴). All of the data were digitized, stored, and processed with a computer. A schematic of the apparatus is shown in Figure 1. The experiment was repeated 5 times under the same test condition and the averaged experimental results were obtained with a relative standard deviation of 0.16%~0.28%.



Figure 1 Schematic diagram of experiment set-up.

3. Results and discussion

Figure 2 shows the flame temperature *vs* time curves origin from the combustion of the modified Ba(NO₃)₂/Mg and ordinary Ba(NO₃)₂/Mg. Table 2 gives the averaged experimental results for the formulations tested.

From Figure 2 and Table 2, we can see that the flame temperature of the ordinary $Ba(NO_3)_2/Mg$ is much higher than the modified $Ba(NO_3)_2/Mg$. It is believed that the flame temperature differences play a significant role in differing luminous intensity¹⁵⁾. However, we were surprised to find that the experimental results were the opposite of what we expected, as shown in Table 2 and Figure 3. We can see that the luminous intensity of the modified $Ba(NO_3)_2/Mg$ system is much higher than the ordinary $Ba(NO_3)_2/Mg$ system.

This may be attributed to the modified $Ba(NO_3)_2$ having a cohesive effect on the sample, resulting in conservation of reaction energy. From the preparation process of the modified $Ba(NO_3)_2^{9)}$, we can see that the modified Ba $(NO_3)_2$ was obtained by adding $0.5 \sim 1.0\%$ NiO, CoO or Cu₂O. On the one hand, because the NiO, CoO, Cu₂O or the other production exist in the modified $Ba(NO_3)_2$, it was



Figure 2 The flame temperature vs time curves.

 Table 2
 Average optical combustion characteristics for ordinary Ba(NO₃)₂/Mg and modified Ba(NO₃)₂/Mg.

No.	Average flame temperature [K]	Average luminous intensity [10 ⁴ cd]	Average burn rate [mm·s ⁻¹]
1	1080	2.59	3.54
2	1258	2.06	4.04
3	1127	2.32	3.66



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Figure 3 The luminous intensity vs time curves for Ba(NO₃)₂/ Mg and modified Ba(NO₃)₂/Mg.

theorized that they will absorb some heat energy when the modified $Ba(NO_3)_2/Mg$ system burns, so that the flame temperature is lower than the ordinary $Ba(NO_3)_2/Mg$ system, as shown in Table 2 (No. 3), and because less heat energy was presumably available to react with the modified $Ba(NO_3)_2/Mg$ system, resulting in a slower burn rate. On the other hand, according to the reference¹⁵, it was found that the luminous intensity of the pyrotechnic mixtures has increased when the some metal oxides were added, and this phenomenon does not follow the optical radiation theory. This phenomenon was referred in the literature¹⁵, but in which little research has been done on this phenomenon.

In order to prove the above viewpoint, the luminous intensity of the burning of the NiO/Ba $(NO_3)_2/Mg$ system and the Ba $(NO_3)_2/Mg$ system (as shown in Table 1) were studied, in which the results are shown in Figure 4.

From Figure 4, we can see that the luminous intensity of the Ba(NO₃)₂/Mg mixtures increased after adding the NiO. It was previously found that metal oxides have very strong effect on the luminous intensity of the reaction system, and that the more solid and liquid particles in the illuminating composition flame, the higher the luminous intensity¹⁵⁾⁻¹⁷⁾. It was also shown that when 2 parts by mass of Al₂O₃ was added to 100 parts by mass of the KClO₄/Al system, the luminous intensity of this system increased 1.41 times¹⁶⁾. Therefore, it is suggested that the presence of metal oxides have increased the luminous intensity of the reaction system.

4. Conclusions

The combustion characteristics of $Ba(NO_3)_2/Mg$ containing pyrotechnic mixtures were experimentally studied for samples containing modified $Ba(NO_3)_2$ and ordinary $Ba(NO_3)_2$. The results have shown that the modified $Ba(NO_3)_2$ lowers the flame temperature and increases luminous intensity for the ordinary $Ba(NO_3)_2/Mg$ system that reacted in air. We propose two general mechanisms to explain this phenomenon. One is that the presence of NiO, CoO, Cu₂O and the other productions in the modified $Ba(NO_3)_2$ will absorb some heat energy from the modified $Ba(NO_3)_2/Mg$ system reaction, thereby



Figure 4 The luminous intensity *vs* time curves for Ba(NO₃)₂/Mg and NiO/Ba(NO₃)₂/Mg.

decreasing the flame temperature and the burn rate. The other is that the presence of NiO, when it is heated up, will increase the luminous intensity of the reaction system. Finally, the mechanisms to explain this phenomenon were confirmed by the burning experiments.

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