Letter

Effect of nitrocellulose and polytetrafluoroethylene on the combustion characteristics of Ba (NO₃)₂/ Mg-containing pyrotechnic mixtures

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Abstract

The examination of nitrocellulose (NC) and polytetrafluoroethylene (PTFE), and their influences on the combustion characteristics of Ba(NO₃)₂/Mg were studied experimentally, using IGA-140 non contact far-infrared thermometer and transient intensity testing instrument. The results revealed that the burn temperature, lumionous intensity and burn rate of the pyrotechnic mixtures with NC (1432.6°C, 49140.3cd, 9.0 mm/s) were all larger than the PTFE system (1248.4°C, 32439.8cd, 7.3 mm/s), which is due to the differences in the decomposition progress between the two additives, so that led to substantial differences in the loss of reaction energy.

Keywords : pyrotechnic mixtures, additives, combustion characteristics

1. Introduction

Pyrotechnics are widely used in military. Two such applications are infrared decoy flares and colored signal flares¹⁾⁻⁶. Many such pyrotechnic flare compositions contain barium nitrate (Ba(NO₃)₂) as oxidizer⁷), and the use of barium nitrate in light-producing compositions has been investigated widely^{8),9}. Magnesium is one of the most common fuels, because of its low price and simplicity to ignite. Nitrocellulose is a derivative of natural cellulose and has an outstanding range of properties. With a nitrogen content above 12.6% it is classed as an explosive¹⁰. The PTFE is a thermoplastic, fluorinated polymer, having an ivory appearance. It has a remarkable applicative potential in various fields¹¹.

Pyrotechnic formulations containing magnesium and barium nitrate, both of them are used for flares pyrotechnic compositions, and have been studied carefully¹²⁾. However, to the best of our knowledge, the comparison study of combustion characteristics between high nitrogen-based additive system and fluorine-based additive system has not been performed. Although additive systems and their influences on burning rates of formulations have been studied by Sabatini, their additive systems were both aromatic hydrocarbon-based¹³⁾. Authors of this manuscript are exploring different additive systems : one is high-nitrogen based nitrocellulose (NC) and the other is carbon-fluorine based polytetrafluoroethylene (PTFE).

The major properties of pyrotechnic compounds are the combustion characteristics. In this research we have started the initial work towards understanding how additives affect the combustion characteristics of standard pyrotechnic mixtures of barium nitrate with magnesium. For this initial study we have chosen as additives substances that are familiar to those working in the pyrotechnics area.

In the present work, NC and PTFE were used as additives. The combustion characteristics of Ba (NO₃)₂/Mg with them were studied experimentally using IGA-140 non contact far-infrared thermometer and transient intensity testing instrument analysis. Results of this work should provide valuable information for select mixtures, which will be used in future studies of additives in these types of pyrotechnic mixtures.

2. Experimental

2.1 Materials

Barium nitrate (Ba(NO₃)₂, pure, mesh 90) was purchased

Table T Composition of samples and weight.						
No.	Ba(NO3)2 [wt %]	Mg [wt %]	NC [wt %]	PTFE [wt %]		
1	59.5	40.5	0	0		
2	56.5	38.5	5	0		
3	56.5	38.5	0	5		

Table 2Average of optical combustion characteristics for Ba
(NO3)2/Mg. with the different additives.

No.	Average burn temperature [℃]	Average luminous intensity[cd]	Average burn rate [mm/s]	Average height [mm]
1	1658.1	65741.2	12.8	14.1
2	1432.6	49140.3	9.0	14.4
3	1248.4	32439.8	7.3	14.2

from Anqiu Hongru Chemical Company (Anqiu, Shandong, China); magnesium (mesh 120) was purchased from Northeast Light Alloy Company Ltd. (Harbin, Heilong-jiang, China); NC with 13.9% N content (NC, pure, mesh 90) was purchased from Sichuan Nitrocell Corporation (Chengdu, Sichuan, China); and PTFE powder (pure, mesh 90) was purchased from Guangzhou City, the new thin Metal and Chemical Company Ltd. (Guangzhou, Guangdong, China).

2.2 Methods

2.2.1 Preparation of samples

The pyrotechnic mixtures, containing Ba $(NO_3)_2/Mg$, Ba $(NO_3)_2/Mg / NC$ and Ba $(NO_3)_2/Mg / PTFE$ are showed in Table 1 with their weight ratios.

The dry chemicals to prepare 30-g batches of the formulations, as shown in Table 1, were weighed out and dried in an oven overnight at 50°C. The chemicals were then individually sifted through a 90-mesh screen. The sifted chemicals were then mixed with their respective binder system and blended by hand for 20 min. After mixing, the mixtures were passed through 40 mesh sieve. The granules were dried in air for 2-3h at ambient temperature to ensure partial curing before consolidation. Mixtures were weighed out in five 15 g increments and pressed into pellet by using a 25-ton-pressure oil pressure machinery under 2MP with a dwell time of 5s, the average height of the pellets were shown in Table 2.

Five pellets of each formulation were pressed and initiated with an electric match at energy of 2V.

2.2.2 Combustion characteristics

The experiment was carried out in a laboratory photometric chamber (darkroom). The burning flame temperature of pyrotechnic mixtures was measured by IGA-140 non contact far-infrared thermometer (The Germany IMPAC Instrument Company), at the same time, the burning luminous intensity of the pyrotechnic mixtures was measured by transient intensity testing instrument (Xi'an Institute of Applied Optics).



Figure 1 Schematic diagram of experiment set-up.

The burn rate of the pyrotechnic mixtures was measured by target lines at constant pressure. All of the data were digitized, stored, and processed with a personal computer. A schematic of the apparatus is shown in Figure 1. The experiment was repeated 5 times at the same testing condition.

3. Results and Discussion

Figure 2 displays a set of the luminous intensity test curve, and Table 2 shows the average of five-times'experimental results under the same testing condition. As shown in Figure 2 and Table 2, the burning rate, the burning temperature and the luminous intensity for the Ba $(NO_3)_2/Mg/NC$ are all higher than the Ba $(NO_3)_2/Mg/NC$ are all higher than the Ba $(NO_3)_2/Mg/NC$ are solved by the same testing Mg/PTFE, and lower than the Ba $(NO_3)_2/Mg$ mixtures.

In order to analyze this phenomenon, the thermal stability of the NC and PTFE used in the formulations was examined by simultaneous DTA-TG in air. The results are shown in Figure 3 and Figure 4 respectively. The TG/DTA curves represent a single sharp exothermic behavior with a maximum at 206.3°C, which is accompanied by a sharp weight loss corresponding to the decomposition of NC¹⁴). However, as seen in Figure 4, there are two endothermic peaks at 337.2°C and 526.4°C, which are ascribed to melting and decomposition of PTFE, respectively. The weight drastically reduced around the decomposition temperature, which means that the thermal stability of the PTFE is far better than NC.

On the other hand, as viewed from their decomposition



Figure 2 Curves for luminous intensity.



Figure 3 TG/DTA curves for NC (sample mass 3.0 mg; heating rate 5°C/min).



Figure 4 TG/DTA curves for PTFE (sample mass 3.0 mg; heating rate 5°C/min).

reaction, the heat output of the NC is 2283.6 J/g, meaning that NC is a typical energetic material. PTFE is chemically and thermally resistant, owing in part to the high energy of the C-F bond¹⁵⁾, so the heat released during the decomposition is lightly negative, and it is a typical temperature and heat-resistant organic material that can be used in the buildings and cable industries as coating materials^{16,17)}.

Another important factor affecting combustion characteristics of the mixtures is the combustion pressure. To gain a further understanding of additive system differences, gas production calculations of the additive systems decomposition were performed. For simplicity purposes, it was assumed that the polymer length of the additives were n=1and the polymer completely oxidized. Therefore, NC was used in the experiment, the combustion reaction formula as follows¹⁸:

$$2C_{24}H_{29}O_{9}(ONO_{2})_{11} = 24CO_{2}+17H_{2}+24CO+11N_{2}+12H_{2}O$$

According to the equation, the amount of gas production per gram NC is approximately 0.04 mol. PTFE used in the experiment based on thermodynamic theory chemical analysis, the decomposition reaction of the equation may be¹¹:

$$\left[CF_2 - CF_2 \right] \stackrel{\bigtriangleup}{\longrightarrow} CF_2 - CF_2 \tag{1}$$

Calculated per gram PTFE gas production is approximately 0.01 mol. Therefore, under the same conditions, the gas pressure was generated by combustion for unit mass of the NC which is approximately 4 times more than PTFE, with lower pressure being produced by the PTFE result in slower burning rate and lower luminous intensity.

It can be seen that NC and PTFE serve as the additives, they typically serve to retard burn temperature, luminous intensity and burn rates by decreasing the overall energy of the Ba (NO₃)₂/Mg system through the inhibition of chemical reactions between adjacent particles. But the thermal stability of the PTFE is far better than NC, and the gas production for unit mass of the NC is more than PTFE, so the reaction of pyrotechnic mixtures with NC is more rapid than PTFE system.

4. Conclusions

In summary, NC-based formulations afforded larger luminous intensity, higher burn temperature and faster burn rate compared to PTFE-based formulation counterparts. This phenomenon was due to significant differences in the decomposition progress between the two additives. Although both are thought as additives, DTA-TG data indicated that NC is a more energetic additive than PTFE. On the other hand, it has been also demonstrated that depending on the used additive system, pyrotechnic formulations could be tuned to accommodate different combustion characteristics (shorter or longer burn times, lesser or larger luminous intensity, and so on).

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