



Effect of Different Binders on the Combustion Characteristics of Ba(NO₃)₂/Mg-containing Pyrotechnic Mixtures

Di-hua OUYANG

*Engineering University of Chinese Armed Police Force,
Xi'an 710086, P. R. China*

E-mail: oydh2013@yahoo.com.cn

Abstract: The combustion characteristics of Ba(NO₃)₂/Mg with binders such as phenolic resin (PR) and nitrocellulose were studied experimentally using an IGA-140 non contact, far-infrared thermometer and transient intensity testing instrument. The results revealed that the burn temperature, luminous intensity and burn rate of the pyrotechnic mixtures with PR (1594.5 °C, 47235.6 cd, 12.5 mm/s) were all larger than the NC system (1432.6 °C, 3242.9 cd, 9.0 mm/s), which is due to differences in the decomposition progress of the two binders that led to substantial differences in the loss of reaction energy and the exothermic reaction between the phenolic resin and the oxidizer before the Mg-oxidizer reaction.

Keywords: binders, pyrotechnic mixtures, luminous intensity, combustion characteristics

Introduction

Pyrotechnics are used in a variety of military applications. Two such applications are infrared decoy flares and coloured signal flares [1-6]. Many such pyrotechnic flare compositions contain barium nitrate, which acts as the oxidizer [7], and the use of barium nitrate in light-producing compositions has been investigated [8, 9]. Magnesium is one of the most common fuels because it is inexpensive and easy to ignite. Pyrotechnic formulations containing magnesium and barium nitrate are used in pyrotechnic illuminating compositions, and have been studied in detail [10]. To the best of our knowledge, no studies

have been done on the combustion characteristics, comparing a hydrocarbon-based binder system and a high-nitrogen-based binder system. Although binder systems and their influence on the burn rates of formulations have been studied, the binder systems studied by Sabatini were both aromatic hydrocarbon-based [11]. The authors of the present paper have explored completely different binder systems, one being high-nitrogen based (nitrocellulose, NC) and the other being hydrocarbon-based (phenolic resin, PR).

The type of binder, as well as the binder content, influences the two main parameters of the redox reactions used in pyrotechnics [12]. In the present work, a phenolic resin (PR) and nitrocellulose (NC) were used as the binders. The combustion characteristics of $\text{Ba}(\text{NO}_3)_2/\text{Mg}$ with these binders has been studied experimentally using an IGA-140 non contact, far-infrared thermometer and transient intensity testing instrument analysis. The results of this work should provide valuable information when selecting mixtures to be used in future studies of binders in these types of pyrotechnic mixtures.

Experimental

Materials

The materials used were barium nitrate ($\text{Ba}(\text{NO}_3)_2$, pure, mesh 90) purchased from Anqiu Hongru Chemical Company (Anqiu, Shandong, China); magnesium (mesh 120) purchased from Northeast Light Alloy Company Ltd. (Harbin, Heilong-jiang, China); phenolic resin (PR, $\text{C}_{48}\text{H}_{42}\text{O}_7$, specific gravity = 1.25, reddish, mesh 90) purchased from Shandong Shengquan Chemical Company Ltd. (Zhangqiu, Shandong, China); and nitrocellulose with 13.9% N content (NC, pure, mesh 90) purchased from Sichuan Nitrocell Corporation (Chengdu, Sichuan, China).

Procedure

Preparation of samples

The pyrotechnic mixtures investigated, containing $\text{Ba}(\text{NO}_3)_2/\text{Mg}$, $\text{Ba}(\text{NO}_3)_2/\text{Mg}/\text{PR}$ and $\text{Ba}(\text{NO}_3)_2/\text{Mg}/\text{NC}$, are shown in Table 1.

Table 1. Composition of samples by weight

No.	$\text{Ba}(\text{NO}_3)_2$ [wt%]	Mg [wt%]	PR [wt%]	NC [wt%]
1	59.5	40.5	0	0
2	56.5	38.5	5	0
3	56.5	38.5	0	5

The dry chemicals required to prepare 20 g batches of the formulations in Table 1 were weighed out and allowed to dry in an oven overnight at 50 °C. The chemicals were then individually sieved through a 90-mesh screen. The sieved chemicals were mixed with their respective binder system (the binders used were dissolved in acetone before being mixed) and blended by hand for 20 min. After mixing, the formulations were passed through a 40 mesh 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 two 10 g portions and pressed into pellets using a manual press and tooling die at a consolidation dead load of 3 MPa with a dwell time of 10 s. The pellets had a diameter of 1.80 cm, a height of 2.50 cm, and weighed 9.94-10.08 g.

Five pellets of each formulation were pressed and initiated with an electric match at an energy of 12 V.

Combustion characteristics measurements

The experiments were performed in a laboratory photometric chamber (darkroom). The burning flame temperature of the pyrotechnic mixtures was measured by an IGA-140 non contact, far-infrared thermometer (The German IMPAC Instrument Company). The luminous intensity of the pyrotechnic mixtures was measured by a transient intensity testing instrument (Xi'an Institute of Applied Optics). The burn rate of the pyrotechnic mixtures was measured by target lines at constant pressure. The flame temperature and the luminous intensity of the pyrotechnic mixtures were measured simultaneously. The data were digitized, stored, and processed with a modified personal computer. A schematic diagram 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 0.10%~0.24%.

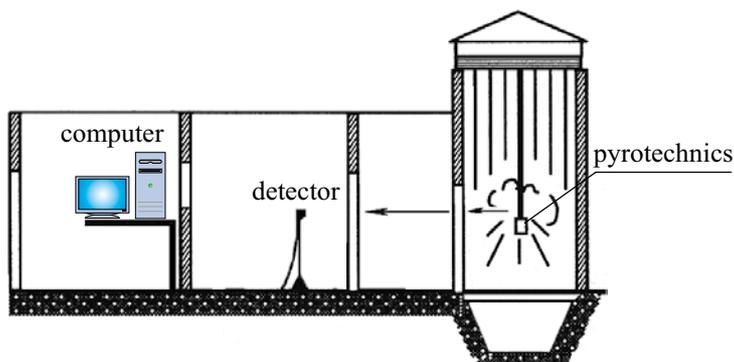


Figure 1. Schematic diagram of the experiment set-up.

Results and Discussion

It is believed that structural differences play a significant role in differing burn rates [11]. To gain an understanding of the binder differences, oxygen balance calculations were performed. For simplicity, it was assumed that the polymer length of the binders was $n = 1$. Therefore, the molecular formula of the phenolic resin (PR) was $C_{48}H_{42}O_7$ and the molecular formula for nitrocellulose was $C_{24}H_{29}N_{11}O_{42}$. Thus the oxygen balance of these two binder systems can be calculated according to the molecular formula given in [11]. For complete combustion of the binder material (*i.e.*, CO_2 and H_2O formation), the oxygen balance of the phenolic resin (PR) binder system was calculated to be -240.1% and the oxygen balance of nitrocellulose -33.4%. Because the oxygen balance of the NC was higher than that of PR, it was theorized that less oxygen was required for complete combustion of the binder material. With less oxygen being consumed by the NC, more oxygen was presumably available to react with the $Ba(NO_3)_2/Mg$ system, resulting in a faster burn rate. However, we were surprised to find that the experimental results were the opposite of what we expected, as shown in Figure 2 and Table 2.

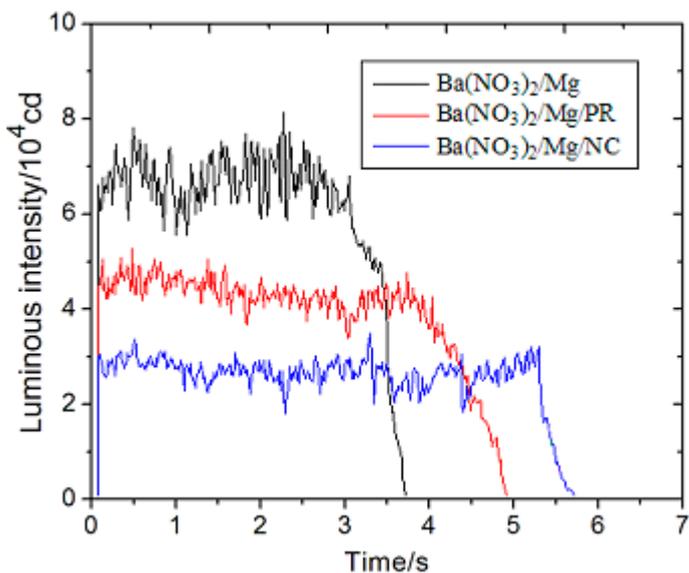


Figure 2. Luminous intensity vs. time.

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

No.	Average burn temperature (°C)	Average luminous intensity (cd)	Average burn rate (mm/s)
1	1658.1	65741.2	16.8
2	1594.5	47235.6	12.5
3	1432.6	32439.8	9.0

Figure 2 shows the luminous intensity *vs.* time curves, and Table 2 gives the averaged experimental results of the formulations tested. As shown in Table 2 and Figure 2, although the decomposition of nitrocellulose at 200 °C [13] is lower than that of the phenolic resin (PR), and the oxygen balance of the NC is higher than that of PR, the burn rate, the burn temperature and the luminous intensity for the Ba(NO₃)₂/Mg/phenolic resin are higher than those for Ba(NO₃)₂/Mg/nitrocellulose.

This may be attributed to the phenolic resin having a cohesive effect on the sample, resulting in conservation of reaction energy. As shown in Figure 3, the cross-linking (or melt) of the phenolic resin is between 50 and 400 °C. The role of this binder ensures that a higher combustion temperature is maintained, which translates to a faster burn rate and a higher luminosity. This is further supported by the literature, as the exothermic reaction between the phenolic resin and Ba(NO₃)₂ occurs before the Mg/Ba(NO₃)₂ reaction, causing a reduction in the ignition temperature [14]. This mechanism was further supported by the DTA curve of the phenolic resin with Ba(NO₃)₂, which gives an onset exotherm at 380 °C, involving a chemical reaction between the free methylene groups obtained from thermal degradation of the phenolic resin and Ba(NO₃)₂ [15].

Nitrocellulose, on the other hand, decomposes rapidly and produces significant amounts of nitrogen gas, which may serve to cool the flame, thus extending the burn time and reducing the luminosity.

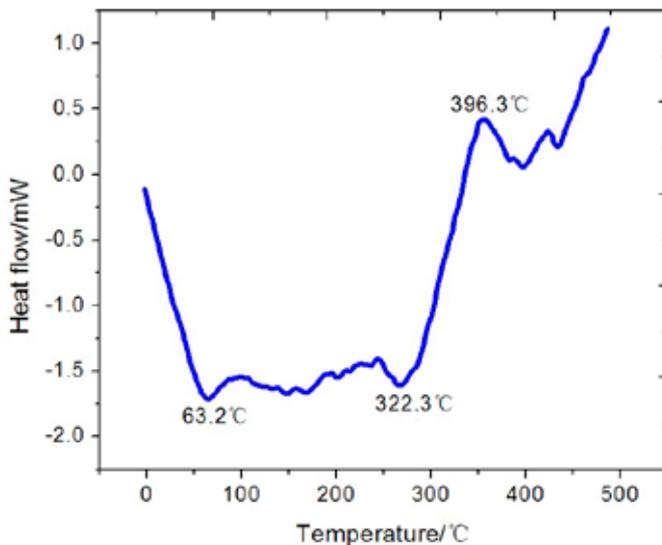


Figure 3. DSC of the phenolic resin.

Conclusions

In summary, phenolic resin-based formulations afforded a higher luminous intensity, a higher burn temperature and a faster burn rate compared to the corresponding nitrocellulose-based formulation. This phenomenon arose due to significant differences in the decomposition progress of the two binders. As a result, substantial differences involving the loss of reaction energy and the exothermic reaction were observed for the phenolic resin and $\text{Ba}(\text{NO}_3)_2$ before the $\text{Mg}/\text{Ba}(\text{NO}_3)_2$ reaction. It was also demonstrated that the oxygen balance has no obvious effect on the combustion characteristics of $\text{Ba}(\text{NO}_3)_2/\text{Mg}/\text{phenolic resin}$ and $\text{Ba}(\text{NO}_3)_2/\text{Mg}/\text{nitrocellulose}$.

Acknowledgements

The authors are grateful to Xin Chen for her help. The project was supported by the National Natural Science Foundation of China (Grant No. 51076066).

References

- [1] Shortridge R.G., Wilharm C.K., Yamamoto C.M., *Elimination of Perchlorate Oxidizers from Pyrotechnic Flare Compositions*, ESTCP 07E-WP3-021, Navsea Warfare Centers, Dec, Crane, Indiana, **2007**.
- [2] Shortridge R.G., Yamamoto C.M., *Perchlorate-Free Red Signal Flare Composition*, US 0132506, **2011**.
- [3] Shortridge R.G., Yamamoto C.M., *Perchlorate-Free Green Signal Flare Composition*, US 7988801, **2011**.
- [4] Yamamoto C.M., Shortridge R.G., *Perchlorate-Free Yellow Signal Flare Composition*, US 0139322, **2011**.
- [5] Sabatini J.J., Nagori A.V., Chen G., *et al.*, High-Nitrogen-Based Pyrotechnics: Longer and Brighter-Burning, Perchlorate-Free, Red-light Illuminants for Military and Civilian Applications, *Chem. – Eur. J.*, **2012**, *18*, 628-631.
- [6] Sabatini J.J., Nagori A.V., Latalladi E.A., *et al.*, Applications of High-Nitrogen Energetics in Pyrotechnics: Development of Perchlorate-Free Red Star M126A1 Hand-Held Signal Formulations with Superior Luminous Intensities and Burn Times, *Propellants Explos. Pyrotech.*, **2011**, *36*, 373-378.
- [7] Klapötke T.M., Radies H., Stierstorfer J., *et al.*, Coloring Properties of Various High-Nitrogen Compounds in Pyrotechnic Compositions, *Propellants Explos. Pyrotech.*, **2010**, *35*, 213-219.
- [8] Conkling J.A., *Chemistry of Pyrotechnics*, Marcel Dekker, New York, **1985**.
- [9] Akhavan J., *The Chemistry of Explosives*, 2nd ed., The Royal Society of Chemistry, London, **2004**.
- [10] Jay C.P., Sabatini, J.J., Comparison of Barium and Amorphous Boron Pyrotechnics for Green Light Emission, *J. Energ. Mater.*, **2013**, *31*(1), 27-34.
- [11] Sabatini J.J., Freeman C.T., Poret J.C., *et al.*, An Examination of Binder Systems and Their Influences on Burn Rates of High-Nitrogen Containing Formulations, *Propellants Explos. Pyrotech.*, **2011**, *36*, 145-150.
- [12] Berger B., Parameters Influencing the Pyrotechnic Reaction, *Propellants Explos. Pyrotech.*, **2005**, *30*(1), 27-35.
- [13] Pourmortazavi S.M., Hosseini S.G., Nasrabadi M.R., *et al.*, Effect of Nitrate Content on Thermal Decomposition of Nitrocellulose, *J. Hazard. Mater.*, **2009**, *162*, 1141-1144.
- [14] Redkar A.S., Mujumdar V.A., Singh S.N., Study on Magnesium-Based Pyrotechnic Composition as A Priming Charge, *Def. Sci. J.*, **1996**, *46*(1), 41-47.
- [15] Bikales N.M., *Plastics, Resins, Rubbers, Fibers*, in: *Encyclopedia of Polymer Science and Technology*, John Wiley & Sons, New York, **1969**.

