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Effect of different additives on the thermal properties and combustion characteristics of pyrotechnic mixtures containing the $KClO_4$/Mg–Al alloy

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ABSTRACT

The thermal properties and combustion characteristics of $KClO_4$/Mg–50%Al, $KClO_4$/Mg–50%Al with additives such as nitrocellulose (NC), urotropine and guanidine nitrate (GN) were studied experimentally using differential thermal analysis (DTA) and thermogravimetry (TG) and closed bomb experiments. The results of DTA–TG analysis revealed that additives could affect thermal stability and the decomposition temperature of $KClO_4$/Mg–50%Al alloy. The order of the ignition temperatures of mixtures (T_i) is KP/Mg–50%Al/urotropine (2#, 557.7 °C) > KP/Mg–50%Al/GN(3#, 553.6 °C) > KP/Mg–50%Al (1#, 538.8 °C) > KP/Mg–50%Al/NC (4#, 536.5 °C). On the other hand, the results of the closed bomb experiments confirm that the combustion pressures were all increased with the addition of additives. The ignition delay times of these mixtures are in the order $KClO_4$/Mg–50%Al (1#) > $KClO_4$/Mg–50%Al/GN (3#) > $KClO_4$/Mg 50%Al/NC (4#) > $KClO_4$/Mg–50%Al/urotropine (2#).

1. Introduction

Potassium perchlorate ($KClO_4$, KP) is a powerful oxidizing agent and decomposes at elevated temperatures to produce oxygen as one of its major products [1]. Pyrotechnic formulations containing magnesium–aluminum alloy (Mg–Al alloy) and potassium perchlorate are used for flash pyrotechnic compositions, fireworks [2,3] and fuel rich propellants [4], because they are easy to ignite. The thermal properties of $KClO_4$/Mg–Al alloy/Ca resinate mixtures have been studied [5]. Urotropine is a white powder that has been used as a stabilizing agent in ADN (ammonium dinitramide) propellants and its thermal properties have been studied [6]. It is well known that some of the most successful commercial flame-retardants for cellulosic materials have been guanidine compounds, which are effective and economical flame-retardants. The thermal degradation of wood treated with guanidine compounds (guanidine phosphate, guanidine carbonate and guanidine nitrate) have been studied [7,8]. 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 explosive [9,10]. The effect of nitrate content on thermal decomposition of nitrocellulose has been studied [11].

Two major properties of pyrotechnic compounds are the quantity of gas released and the stability of the compound towards ignition. In this research we have started the initial work towards understanding how additives affect the stability and gas production of standard pyrotechnic mixtures of potassium perchlorate with magnesium–aluminum alloy. For this initial study we have chosen as additives substances that are familiar to those working in the pyrotechnics area. These substances have characteristics that can produce stability in pyrotechnic materials (urotropine and guanidine nitrate) and can add to the production of gaseous products (nitrocellulose).

In the present work, urotropine, guanidine nitrate and nitrocellulose were used as additives. The reaction behavior of $KClO_4$/Mg–50%Al alloy with them has been studied experimentally using differential thermal analysis (DTA) and thermogravimetry (TG) and closed bomb analysis. This was done in order to examine the influence of additives on the thermal properties and combustion characteristics of $KClO_4$/Mg–Al alloy. Results of this work should provide valuable information for selecting mixtures to be used in future studies of additives in these types of pyrotechnic mixtures.

2. Experimental

2.1. Materials

The materials used were potassium perchlorate ($KClO_4$, pure, mesh 300) purchased from Richem Company Ltd. (Beijing, China); magnesium–aluminum alloy (Mg–50%Al alloy, Mg-50%, Al-50%, mesh 300) purchased from Northeast Light Alloy Company Ltd.

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Table 1
Composition of samples.

No.	KP (wt%)	Mg–50%Al (wt%)	Urotropine (wt%)	GN (wt%)	NC (wt%)
1	60	40	0	0	0
2	54.5	36.4	9.1	0	0
3	54.5	36.4	0	9.1	0
4	54.5	36.4	0	0	9.1

(Harbin, Heilong-jiang, China); urotropine (pure, mesh 240) purchased from Zhengzhou Jinfengda Chemical Products Company Ltd. (Zhengzhou, Henan, China); guanidine nitrate (GN, pure, mesh 240) purchased from Jiangsu Qiangsheng Chemical Company Ltd. (Suzhou, Jiangsu, China); and nitrocellulose (NC, pure, mesh 240) purchased from Sichuan Nitrocell Corporation (Chengdu, Sichuan China).

2.2. *Procedure*

2.2.1. *Preparation of samples*

The pyrotechnic mixtures studies, containing KP/Mg–50%Al, KP/Mg–50%Al/NC, KP/Mg–50%Al/urotropine, and KP/Mg–50%Al/GN are show in Table 1 with their weight ratios. The $KClO_4$ and Mg–50%Al alloy used were sieved through 300 mesh. The other additives used were sieved through 240 mesh before being mixed. Pyrotechnic mixtures of $KClO_4$/Mg–50%Al alloy with different additives (in Table 1) were prepared by carefully sieving small quantities of the components through a slightly coarser sieve than 240 mesh, after which the mixtures were further mixed in a glass lined powder mixer until homogeneity was achieved.

2.2.2. *Thermal analysis measurements*

A thermo-balance (Stanton, Model TR-01, with a sensitivity of 0.1 mg, with a differential thermal analysis (DTA) attachment) was used to investigate the thermal properties (DTA–TG) of the samples. In this study, the heating rate was 10 °C/min in air at 1 bar and the sample weight for each analysis was 5.0 mg. α-Al_2O_3 was used as the reference material for calibration of the equipment. The crucibles were not covered. The DTA–TG apparatus was calibrated with standard samples [12] (indium was used for low temperature phase, quartz was used for middle temperature phase, strontium carbonate was used for high temperature phase). In order to investigate the reproducibility of the thermal characteristics for $KClO_4$/Mg–50% Al alloy with additives, the results were recorded three times for each composition and then averaged.

2.2.3. *Closed bomb measurements*

The combustion pressures of pyrotechnics in the closed bomb (its volume is 50 mL) were recorded in air with a pressure transducer (American PCB Company, type is M102B, sensitivity is 143.96 mV/MPa). The closed bomb was developed according to the verification regulation for measuring system of closed bomb for propellants [13]. The closed bomb is constructed of refractory steel. The closing bolt and the deaden plug are made of the same steel. The threads were sealed with a polyurethane sealant. The nichrome wires were insulated and sealed in bolt with 502 sealant. Each sample (0.500 g) was weighted into a paper tube (H = 20 mm, R = 5 mm) and consolidated using a ram under hand pressure and placed into the closed bomb. The sample was ignited by electrically heating a coil of nichrome wire buried in the composition at the center of the tube. The schematic diagram of closed bomb apparatus is shown in Fig. 1. The measurements were recorded three times for each composition and then averaged.

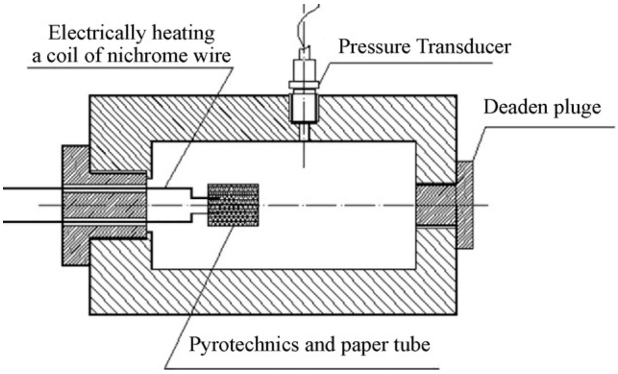


Fig. 1. Schematic diagram of closed bomb apparatus.

3. Results and discussion

3.1. *Thermal behavior of compounds*

3.1.1. *Thermal behavior of the individual components*

The thermal behavior of pure $KClO_4$ has been previously reported [14,15]. The oxidation characteristics of the Mg–50%Al alloy were studied by simultaneous DTA–TG in air. The results are shown in Fig. 2. It can be seen that the melting point of Mg–50%Al alloy is 461.5 °C and there is evidence of a two-stage oxidation process. It is expected that the Mg component of the alloy oxidizes preferentially. There are reports in the literature to this effect. This is due to the higher reactivity of the magnesium with oxygen compared to aluminum [16,17]. The results observed for the Mg–50%Al are similar in nature to those found by Pourmortazavi et al. [11] in their study of Al powders. The results in the current study have two additional features. First, near 461.5 °C there is an endothermic peak that corresponds to the melting of the Mg–50%Al alloy. Second, there is a double peak that corresponds to a two-stage oxi-

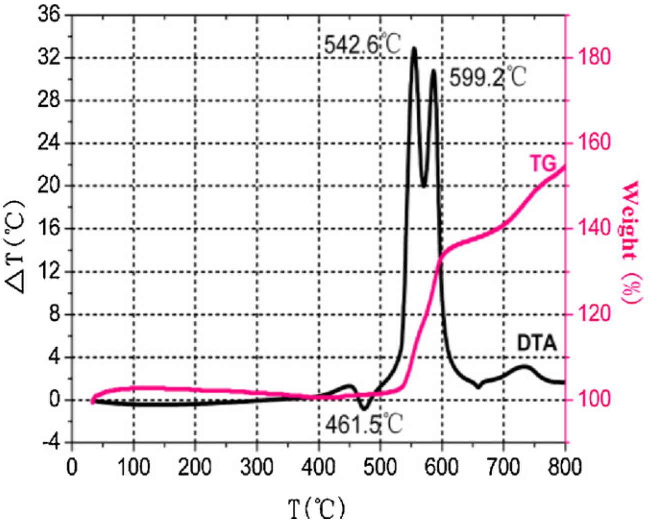
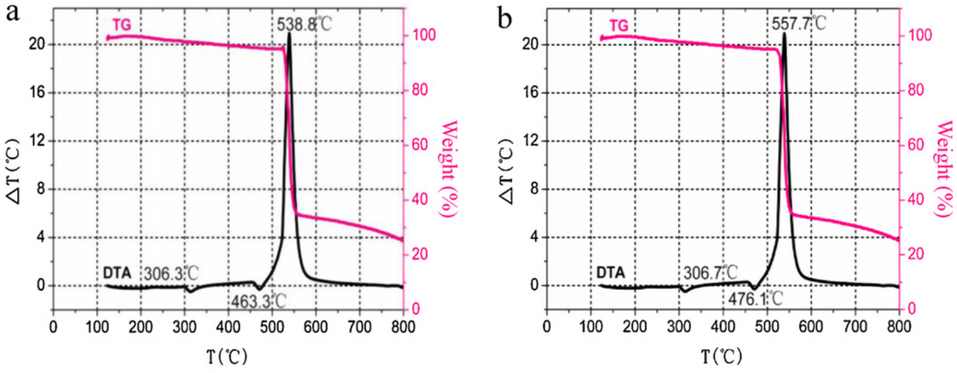
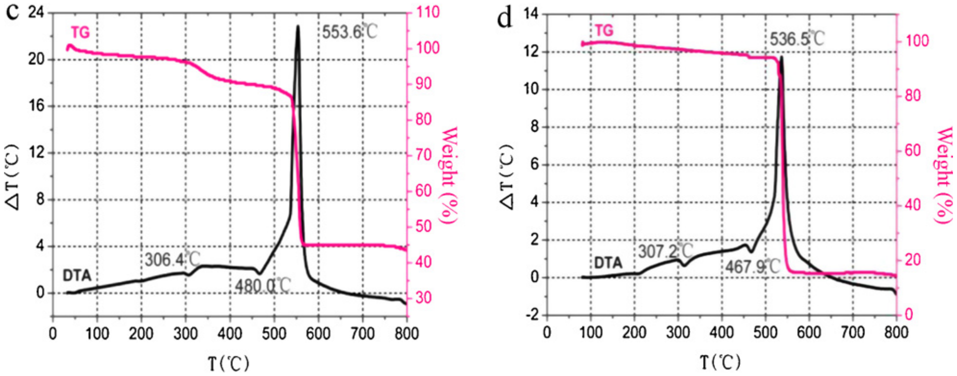


Fig. 2. DTA and TG curves for Mg–50%Al alloy (50–50%).



1# -KP/Mg-50%Al

2# - KP/Mg-50%Al/urotropine



3# -KP/Mg-50%Al/ GN

4# - KP/Mg-50%Al/NC

Fig. 3. DTA and TG curves for mixtures.

dation of the alloy. These peaks are in the same temperature range as that found by Pourmortazavi et al. [11] for the oxidation of pure Al powders. The oxidation of the Mg begins below 540 °C and peaks at 542.6 °C. This is to be expected, as Mg is more reactive in air than Al. The Al oxidation process peaks at approximately 599 °C. While this temperature is higher than that obtained by Pourmortazavi et al. [11], it is consistent with their study of Al powders. All of this reasonably speculative as the work cover here deals with an alloy of two metals. The process of oxidizing an alloy which is in the liquid phase is a much more complicated process than just oxidizing pure component powders. In addition, the alloy is in the liquid state at the point of oxidation with the air. This alloy has a complex phase diagram, so as the Mg is oxidized the liquid alloy will become richer in Al. The liquid phase will also have the oxide of Mg dispersed in it. The explanation given here for a two-stage process seems at least plausible but is recognized as being highly speculative.

3.1.2. Thermal behavior of the mixtures

Fig. 3 shows TG and DTA curves for KP/Mg–50%Al alloy mixture in the pure form and with various additives.

DTA and TG curves for the pure KP/Mg–50%Al alloy mixture are shown in Fig. 3a. An endothermic peak in the DTA curve at 306.3 °C corresponds to a rhombic-cubic transition of KP [14]. The DTA curve also shows an endothermic peak at 463.3 °C, which corresponds with the temperature of fusion of KP. A sharp exotherm occurs near 538.8 °C accompanied by a reduction (about 61.2%) in the mass of sample that corresponds to the oxidation of the Mg–50%Al alloy by the KP according to:

$$5KClO_4 + 8Mg\text{–}Al \rightarrow 8MgO + 4Al_2O_3 + 5KCl$$

A rough calculation shows that complete decomposition of KP and complete oxidation of the alloy (1#: KP: Mg–50%Al = 6:4, assumed uniform for Al and Mg, for simplicity) would result in a ∼17.4% weight increase. Decomposition without oxidation of the alloy would result in a ∼27.6% weight loss. But the observed 61.2%, it could indicate that some material was carried out of the crucible.

Fig. 3b shows the DTA–TG results for the KP/Mg–50%Al/urotropine mixture. There is an endothermic peak at 306.7 °C corresponding to a rhombic–cubic transition of the KP. Then, an endothermic peak occurs at 467.1 °C due to the melting of the KP. An exothermic peak with a decrease in the mass (about 48.7%) occurs at 536.5 °C, which corresponds to the reaction of Mg–50%Al and urotropine with the KP. A rough calculation shows that complete decomposition of KP, complete oxidation of the alloy and urotropine would result in a ∼15.8% weight increase. Decomposition without oxidation of the alloy would result in a ∼34.2% weight loss. But the observed 48.7%, it also could indicate that some material was carried out of the crucible.

In the DTA and TG curves for KP/Mg–50%Al/GN mixture (Fig. 3c), there are endothermic peaks at 306.4 °C, which corresponds to the rhombic–cubic transition of the KP, and at 480.0 °C due to the melting of the mixture. At the same time, we can see that an intense decomposition occurred at about 553.6 °C from the reaction of Mg–50%Al and GN with the KP, which corresponds with a decrease in the mass (about 44%). it may be some material was carried out of the crucible or vaporized from the crucible.

Fig. 3d shows DTA and TG curves for the sample of KP/Mg–50%Al/NC. Two endothermic stages were observed at 306.7 °C and 476.9 °C, corresponding to a rhombic–cubic transition and the melting point, respectively. Next there is an exothermic peak at 536.5 °C with a reduction (about 74.7%) in the mass of sample that corresponds to the reaction of the Mg–50%Al alloy and NC with the KP. It also could indicate that some material was carried out of the crucible or vaporized from the crucible.

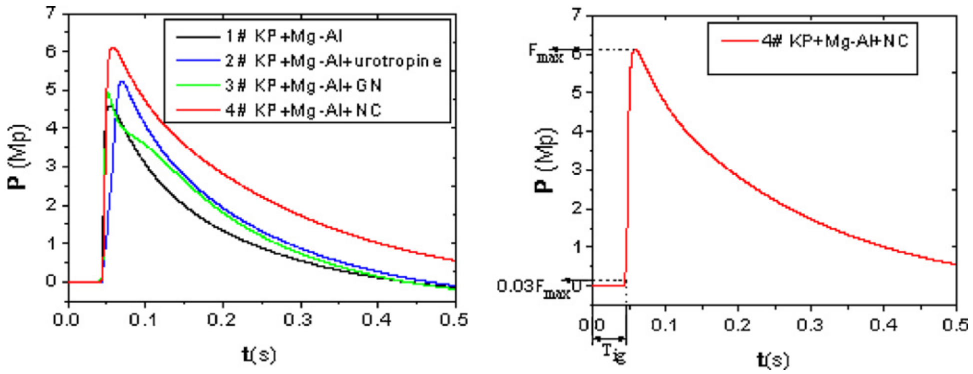


Fig. 4. Curves for pressure (0.500 g).

On the other hand, GN and NC cannot really stable up to 500 °C, because the thermal decomposition of NC and GN are ∼200 °C (it is affected by its particle size and so on). This can be seen from Fig. 3(c) and (d), that their DTA curve are raising and the TG curve are spiral downward before the 500 °C, but the other DTA curve (e.g. (a) and (b)) are horizontal. Because the decomposition of NC and GN that cause the ΔT raised.

The results of these experiments are summarized in the table below.

3.2. Pressure characteristics of mixtures

Pressure is an important parameter in the combustion of pyrotechnics. It can provide information about the degree and intensity of reaction. In this work, the combustion pressure of mixtures of KP/Mg–50%Al with different additives in a closed bomb were measured using a pressure transducer as show in Fig. 4.

As shown in Fig. 4 we can see that the combustion pressures of all KP/Mg–50%Al alloy mixtures increased after adding the different additives. For the mixture of KP/Mg–50%Al (1#) the maximum combustion pressure (P_{max}) is 4.58 MPa. Also the result of the closed bomb experiment for KP/Mg–50%Al/NC (4#) mixture shows this mixture has a maximum pressure of (6.10 MPa). This may be related to the decomposition mechanism of the components in this mixture. For example, a rough calculation shows that complete oxidation of the mixture KP/Mg–50%Al/NC (4#) would result in a P_{max} of 7.42 MPa (perfect gas, $pV = nRT$) gas. The recorded 6.10MPa can be matched with an assumed ∼72.1% oxidation of the mixture (4#). This incomplete reaction may be due to the lack of oxygen resulting in the NC not being completely oxidized. For the two other mixtures, KP/Mg–50%Al/urotropine (2#) and KP/Mg–50%Al/GN (3#), the P_{max} are 5.23 MPa and 4.92 MPa, respectively. The maximum pressures are lower for urotropine or GN as the quantity of gas produced is less than that for the same weight of NC. In the same manner, we can determine the degree of oxidation for the mixtures (2#) and (3#).

From Fig. 4 we also can observe that the ignition delay times (T_{ig}, the time for the pressure to increase to 3% of the maximum pressure). As an example, the T_{ig}, P_{max} and 0.03 P_{max} of 4# are shown in Fig. 4. The igniter was triggered at $t = 0$ s. The magnitudes of the T_{ig} of these mixtures are in the order 1# > 3# > 4# > 2#. This is because the additives need oxygen when they are reacting, but the oxygen which is produced by the KP decomposition is limited such that the Mg–50%Al will not react completely. On the other hand, the additives will absorb heat and this may also decrease the reaction rate. Also, this can be proven from Fig. 5 since the pressure variation speed (dp/dt) decreased, especially for KP/Mg–50%Al/urotropine mixture (2#).

3.3. Ignition temperatures of mixtures

In this study, the thermal behavior of several pyrotechnic mixtures containing Mg–50%Al as fuel, KP as oxidizer and urotropine, GN, NC as additives was studied under identical conditions. For the mixture of KP/Mg–50%Al, as seen in Fig. 3a, the ignition reaction occurred at 538.8 °C. The ignition temperature was decreased to 536.5 °C by the addition of NC to the KP/Mg–50%Al mixture, thus demonstrating an increased sensitivity of this mixture to heat. However, by replacing the NC with GN in this mixture, the sensitivity was decreased and the ignition occurred at 553.6 °C. Comparison of the two mixtures (see Table 2) shows that KP/Mg–50%Al/ GN is more stable than KP/Mg–50%Al/NC and has an increased ignition

Table 2
Summary of results.

No.	T_i (°C)	Average	P_{max} (MPa)	Average	T_{ig} (s)	Average
1# – Test 1	540.1	538.8 °C	4.60	4.58 MPa	0.0455	0.0453 s
1# – Test 2	538.6		4.59		0.0452	
1# – Test 3	537.7		4.55		0.0452	
2# – Test 1	559.5	557.7 °C	5.25	5.23 MPa	0.0445	0.0447 s
2# – Test 2	557.8		5.22		0.0446	
2# – Test 3	555.8		5.22		0.0450	
3# – Test 1	555.0	553.6 °C	4.98	4.92 MPa	0.0448	0.0449 s
3# – Test 2	553.7		4.90		0.0448	
3# – Test 3	552.1		4.88		0.0451	
4# – Test 1	537.0	536.5 °C	6.14	6.10 MPa	0.0442	0.0443 s
4# – Test 2	536.6		6.10		0.0441	
4# – Test 3	535.9		6.06		0.0446	

1# 95% confidence intervals: 534.6–543.0 (T_i); 4.49–4.67 (P_{max}); 0.0448–0.0458 (T_{ig}).
2# 95% confidence intervals: 551.2–564.2 (T_i); 5.18–5.28 (P_{max}); 0.0438–0.0456 (T_{ig}).
3# 95% confidence intervals: 548.5–558.7(T_i); 4.74–5.10 (P_{max}); 0.0444–0.0454 (T_{ig}).
4# 95% confidence intervals: 534.6–538.4 (T_i); 6.00–6.24 (P_{max}); 0.0436–0.0450 (T_{ig}).

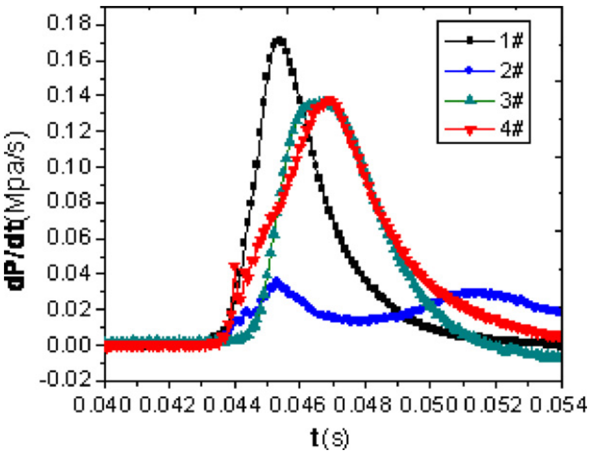


Fig. 5. Curves for pressure variation speed.

temperature of 14.8 °C above that of the pure KP/Mg–50%Al without additives.

By replacing of GN with urotropine, the thermal stability of the pyrotechnic mixture is increased further. The ignition temperature of the mixture of KP/Mg–50%Al/ urotropine is increased to 557.7 °C. For this mixture, the ignition temperature is ~18.9 °C higher than the pure KP/Mg–50%Al mixture.

The relationship of ignition temperatures (T_i) of these mixtures is observed to be in the following order KP/Mg–50%Al/urotropine (2#, $T_i = 557.7$ °C) > KP/Mg–50%Al/GN (3#, $T_i = 553.6$ °C) > KP/Mg–50%Al (1#, $T_i = 538.8$ °C) > KP/Mg–50%Al/NC (4#, $T_i = 536.5$ °C).

4. Conclusions

Thermal behavior and combustion characteristics of pyrotechnic mixtures of $KClO_4$/Mg–50%Al alloy in a pure form and with the different additives were studied by DTA–TG and closed bomb methods. The results show (see Table 2) that with the addition of additives the combustion pressure is increased in the order KP/Mg–50%Al/NC (4#) > /Mg–50%Al/ urotropine (2#) > KP/Mg–50%Al/GN (3#) > KP/Mg–50%Al (1#), but the order of ignition delay time (T_{ig}) for these mixtures is KP/Mg–50%Al (1#) < KP/Mg–50%Al/GN (3#) < KP/Mg–50%Al/NC (4#) < KP/Mg–50%Al/ urotropine (2#). The order of the ignition temperatures of the mixtures (T_i) is KP/Mg–50%Al/ urotropine (2#, 557.7 °C) > KP/Mg–50%Al/GN (3#, 553.6 °C) > KP/Mg–50%Al (1#, 538.8 °C) > KP/Mg–50%Al/NC (4#, 536.5 °C).

This study of pyrotechnic compositions is important not only for understanding the characteristics of their thermal decomposition, but also for assessing the degree to which additives can affect their exothermic decomposition and ignition temperatures. This information can lead to pyrotechnic compositions with improved characteristics to mitigate potential hazards during handling, usage, storage, and to knowledge on how to improve the sensitivity of igniter compositions and reduce factors for accidents.

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