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INVESTIGATION OF THE WATER CONTENT EFFECT ON PRIMER MIXTURES SELF-IGNITION PARAMETER

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The thermal decomposition properties of primer mixture 1 with different water content can be investigated using a series of thermal analysis equipment and by its technique. By the DSC analysis in this work, although the major exothermic peak of the primer mixture 1 with different water content, at the temperature range from 250 to 350°C were gradual disappeared when increasing the water content of primer mixture 1, but this result could not indicate that the detonating ability of wetted primer mixture 1 was lost. And by TG analysis, wetted primer mixture 1 was still found possessing detonation properties under a higher heating rate condition. Although wetted primer mixture shows hard detonating character but we still need very carefully when executing a disposal mission.

Keywords: *self-ignition parameters, water content effect on primer mixtures*

Introduction

Ignition modulus of Electro-Explosive Devices (EED's) has being installed in missile weapon system [1] up to 95% for a long time, and a fuse head of pyrotechnic, such as detonators, initiators, gas generators or battery igniters are always ignition the primer mixtures/or the first fire compositions which was neighboring the bridgewire firstly by input an electric energy. When an electric energy was transmitted in a bridgewire, the heat will release from the bridgewire, then the primer mixtures was ignited when they absorbed enough heat from bridgewire system by radiation or conduction. Primer mixtures are extremely sensitive and relatively easy to explode /or to ignite, as the name suggests, they are used to start the initiation of explosive trains. When primer mixture ignited, they produce an intense local blow of gases and they are not suitable for doing work in blasting operations, usually they are loaded in small quantities into metal (usually copper or aluminum) tubes to form electro-explosive devices, and in this form they are used to ignite base charge of a more powerful high explosives. The EED's that instillation in missile or rocket weapon system have to suffer the thermal shock from the skin of missile/or rocket by conduction that inducing by aerodynamic, especially in high speed missile, the heat will conducting from the skin of missile by friction with air during navigation. And if the primer mixture that used in EED's was sensitive to heat, it may be inducing an explosion accident during launch or navigation. On the other hand, when a sub-munition was spread out to a field /or in a sea, a part of sub-munition may be misfire. In the case, hermetic sealing properties or the water resistance and moisture penetration resistance of sub-munition become extremely important, owing to the firing characteristics and the safety condition of a sub-munition that either after dipped in sea or in water, or for a period/exposed at environments will be considered firstly before executing a disposal mission. In general, although the amount of primer mixture/or ignition composition for a typical detonators/or a initiators was usually small by comparing the amount of base charge, but the threshold of firing energy are really low, the firing characteristics after exposed at environments are really very important in disposal and the hazard factors are extremely complicated. But both of them are all very important in disposal. In this work, the effect factors on thermal properties, decomposition kinetic parameters of primer mixture was evaluated by a series of thermal analysis techniques using TG/DSC, and also by auto-ignition temperature, explosion temperature test equipments. Furthermore, attempting to get more information on decomposition of wetted primer mixture was also investigated by using thermal analysis data of DSC/TG.

Experimental

The compositions of primer mixture that investigation in this work were listed in Table 1, the raw materials

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Table 1 Compositions of primer mixtures

Composition	Primer mixture 1 (#130)	Primer mixture 2 (new primer)
Lead stephnate	40%	
Tetrazene	5%	
Lead azide	20%	28.3%
Sb_2S_3	15%	33.3%
$Ba(NO_3)_2$	20%	
SiC		5%
$KClO_3$		33.4%

were weighted respectively then get a well mixed by repeat brushing the ignition composition to an uniform color carefully. Dm 55 was the detonating mixture obtained from M77 sub-munition. For study the thermal properties of primer mixture, approximately 5 mg samples were measured using Du Pont TA 2000 system with 951 TG and 910 DSC under a static air atmosphere with 5 to 50°C min^{-1} heating rate. A Julius Peter Corporation equipment, 10–15 g primer mixture have been used to measure the auto-ignition temperature with a 5°C min^{-1} heating rate and the explosion temperature within 5 s for primer mixture, the testing specification of MIL-STD-650-T514.1, MIL-STD-650-T515.1 were introduced in this work.

Results and discussion

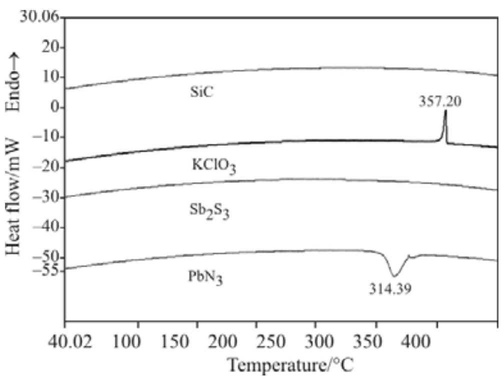

Fig. 1 DSC curves of ingredients for primer mixture 2, under static atmosphere, with a 10°C min^{-1} heating rate

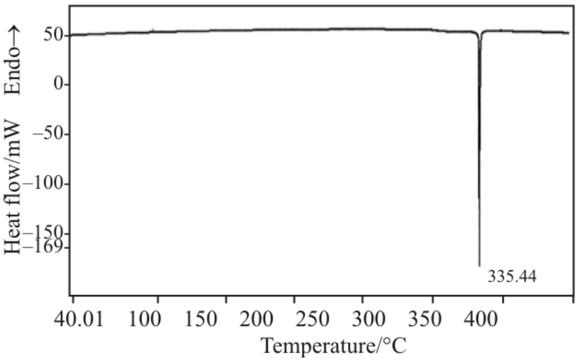

Fig. 2 DSC curves of primer mixture 2, under static atmosphere, with a 10°C min^{-1} heating rate

Figure 1 shows the DSC curves of each ingredients for primer mixture 2, under static atmosphere and with a 10°C min^{-1} heating rate. Only lead stephnate possessed a broad exothermic peak at 314.4°C and potassium chlorate appeared a sharp endothermic peak at 357.2°C. Both SiC and Sb_2S_3 gave either no exothermic peak or endothermic peak in DSC curves. The DSC curve of primer mixture 2, under static atmosphere, with a 10°C min^{-1} heating rate was shown in Fig. 2, primer mixture 2 indicated a very sharp exothermic peak at 335.4°C, this result represents that the decomposition reaction of primer mixture 2 will occur suddenly at an elevation temperature condition, but the exothermic peak temperature of primer mixture 2 was shift to higher temperature than that of lead stephnate. The DSC curves of the primer mixture that with different water content, under static air atmosphere and with a 10°C min^{-1} heating rate are shown in Fig. 3, the DSC curve of primer mixture 1 without water content exhibits two exothermic peaks between 100 and 200°C, following by a sharp exothermic peak appeared at higher temperature ranged from 200 to 300°C and accomplishing a small exothermic peak at the temperature between 500 and 600°C. The first and second exothermic peaks that appeared at 149.2 and 168.4°C respectively, were the characteristic decomposition temperature of tetrazene. According to the earlier researcher [1–3], the curve of tetrazene in DSC, possessed two exothermic peaks at 154 and 179°C respectively, under static air atmosphere and with a 10°C min^{-1} heating rate, the result of DSC in this investigation was close to the earlier study. In order to decrease the thermal sensitivity of primer mixture, then we withdraw tetrazene from the ingredient of primer mixture 1 firstly. Also in DSC curve, the third exothermic peak of primer mixture 1 that between 200 to 300°C was the characteristic decomposition peak of lead stephnate, in the same time, lead azide may be also decomposition in this temperature range, especially at a higher heating rate. The fourth exothermic peak of primer mixture 1 which is above 500°C, was the decomposition temperature of barium nitrate. In primer mixture 1, the detonation of primary explosive would take place firstly when heated the primer mixture, and the oxidizer such as barium nitrate and Sb_2S_3 seem to play a diluter, but the performance of catalyst was not obvious in this study. In Fig. 2, the DSC curve of primer mixture 2 only

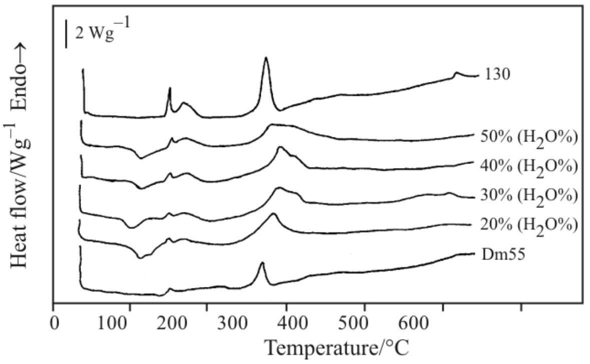

Fig. 3 The DSC traces of primer 1, primer 2 and primers that with different water content, under static air atmosphere and with a 10°C min^{-1} rate

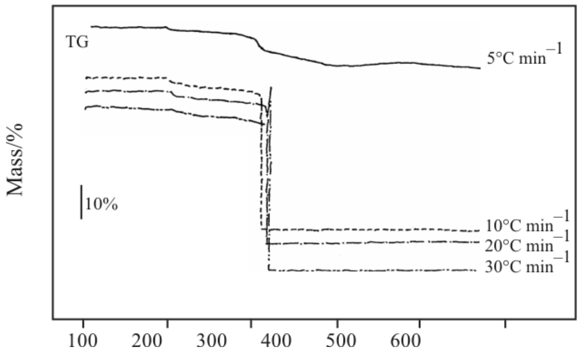

Fig. 4 The TG curves of primer mixture 1 without water content, under static air atmosphere and with 5–30°C min^{-1} heating rate

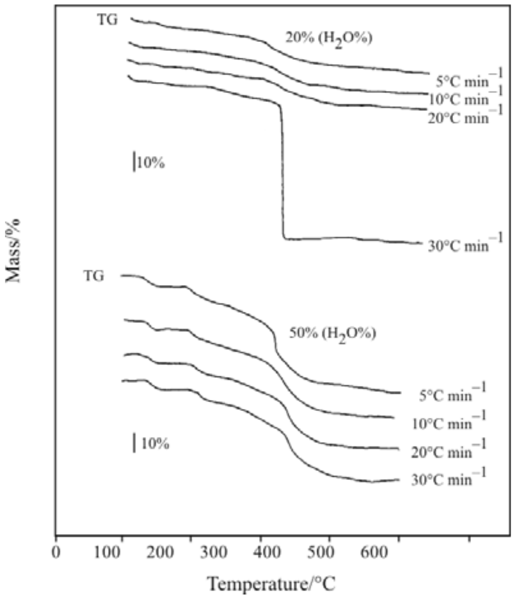

Fig. 5 The TG curves of primer mixture 1 with different water content, under static air atmosphere and with 5–30°C min^{-1} heating rate

show one very sharp exothermic peak between 300 and 400°C, this exothermic peak was major produced by decomposition of lead azide. The thermal analysis of lead azide was already conducted by Lan *et al.*, [4] it was reported that the lead azide appeared decomposition peaks at 326.9 and 330°C, and the activation energy of decomposition of lead azide that calculation by explosion temperature *vs.* time was 159.6 kJ mol^{-1} and the auto-ignition temperature was between 320 to 360°C. The temperature of first exothermic decomposition peak of primer mixture 1 and primer mixture 2 are extremely different, and the decomposition temperature of primer mixture 2 gave at least 150°C higher than that of primer mixture 1, then we are offering the opinion that primer mixture 2 possessed better thermal resistibility than that of primer mixture 1. On the other hand, the DSC curves in Fig. 3, the primer mixtures with different water content, the endothermic peak was found when the temperature excess 100°C, following by a coupling broad exothermic peak (100–200°C), and the another broad exothermic peak was appeared around 300°C, both of above broad exothermic peaks for primer mixtures with different water content trend to lower temperature and being flat, this result indicated that the rate of decomposition reaction in wetted primer mixtures become slow (or low order reaction) and may be loss the detonation characteristic already. Dm55 also shown a similar DSC curve with primer mixture 1, the ingredients of primer mixture 1 are closed Dm55.

Although at higher heating rate, DSC curves of the primer mixture with different water content shown no any detonation characteristic, and the rate of decomposition reaction of primer mixtures with different water content would decrease by increasing the water content of primer mixture, this result could not indicate detonation was occurred. Hence the important factor of water content in a primer mixture was hard to evaluate only using DSC analysis.

The TG curves of primer mixture 1 and primer mixtures containing different water contents under static air atmosphere with 5–30°C min^{-1} heating rates are shown in Figs 4 and 5. For the primer mixture 1 which is without water content, when the lower heating rate (e.g. 5°C min^{-1}) was hold in TG analysis, the TG curve only shown decomposition, the mass loss percentage increased slowly with elevating temperature. But when TG running in the higher heating rate (e.g. up 10°C min^{-1}), the mass loss percentage of TG curves was increased suddenly around 300°C, this phenomenon means that primer mixture 1 occurs detonation reaction by ignition the lead stephnate. The detonation phenomenon of TG result for primer mixture 1 was out of DSC curves observing, the detonation phenomenon of primer mixture 1, containing low percentage of water only occur at fast heating rate (e.g. 20% water content, at 30°C min^{-1} heating

Table 2 Firing characteristics, kinetic parameters of primary explosive and primer mixtures

Explosives/primer mixtures	Auto-ignition temperature/°C	E_a of auto-ignition/kJ mol^{-1}	Explosion temp./°C
Lead azide	300	343.17, R^2=0.9975	320–360
Lead stephnate	256	233.27, R^2=0.9742	275–282
Primer mixture 1	137	115.5, R^2=0.9843	174.1
Primer mixture 2	273	130.9, R^2=0.9881	293.2

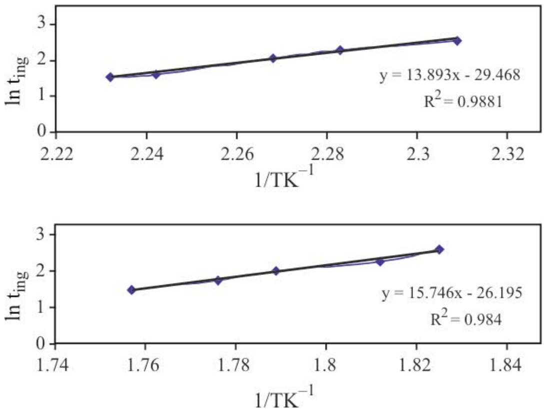

Fig. 6 Evaluation the activation energy of auto-ignition for primer mixture 1 and primer mixture 2 by plotting ln$t$ *vs.* 1/T

rate), that is detonation took place in the primer mixture 1 (mass loss percentage increased suddenly with elevating temperature), but in the others TG curves, the primer mixture containing water content (e.g. 50% water content), they are all appeared decomposition reaction (mass loss percentage of primer mixture 1 increased slowly with elevating temperature). In fact, we recommend water played an extremely non-detonation role in primer mixture 1, but we still have to take carefully in disposal of the wetted explosives or wetted primer mixture ingredients.

Thermal analysis is a useful technique to characteristic explosive [3–16] and the non-isothermal DSC/DTA/TG technique that using a series heating rate method could introduce a quickly and simply route to get the kinetic parameters of relative reaction. Table 2 showns the decomposition activation energy of primer mixture 1 and primer mixture 2, the value of decomposition activation energy for primer mixture 2 was obtained by plot ln$t$ *vs.* 1/T (Fig. 6) and it was just a litter higher than that of primer mixture 1. The measurements of time to ignition have provided to be a popular route to get chemical activation energy of explosives, propellants and pyrotechnics. But it is often assumed in an adiabatic condition, and for the purpose of modeling and estimating safety that deflagration is described by a first order Arrhenius equation. Experimentally, it is found that many energetic materials appear to obey such a law, except for a region at long ignition delays [17]

$$\ln T = E_a/RT + \text{constant} \tag{1}$$

where E_a is the activation energy in the above equation using the adiabatic approximation, R is the gas constant and T is temperature that hold in experimental, T is the time constant inversely proportional to reaction rate. The auto-ignition temperature and explosion temperature of primer mixture 1 and primer mixture 2, lead azide, lead stephnate are also listed in Table 2, primer mixture 2 always posseses higher auto-ignition temperature and higher explosion temperature than that of primer mixture 1, this result also indicate that primer mixture 2 possessed better thermal resistibility than that of primer mixture 1.

Conclusions

The ingredients of primer mixture can be selected and constructed the right composition effectively by a series of thermal analysis and it’s technique, and the thermal characteristics of pyrotechnics and explosives can also builded up quickly by thermal analysis equipments. The relative kinetic parameters of thermal analysis are regarded as the evidence of degradation and de-sensitive for primer mixture. In this work we withdraw the thermal sensitive explosive from the ingredients of primer mixture 1 after reviewing the thermal analysis data, and a new primer mixture that possessed better heat resistibility was prepared, then examined using thermal analysis techniques. No matter the temperature of exothermic peak in DSC curve, or auto-ignition temperature, explosion temperature for primer mixture 2 were higher than that of primer mixture 1, the goal of this work was accomplished. The detonating characteristics of wetted primer mixtures were also screened using thermal analysis techniques. Finally, the thermal resistibility of primer mixture 1 was evaluated and the aim of this work was accomplished. Although wetted primer mixture shows hard detonating character but we still need very carefully when executing a disposal mission.

References

1 T. Urbanski, Chemistry and Technology of Explosives Vol. III (1967) 208.
2 T. Urbanski, Chemistry and Technology of Explosives Vol. III (1967) 215.
3 T. Urbanski, Chemistry and Technology of Explosives Vol. III (1967) 172.
4 D. Haishan, H. Rongzu, Y. Pu and C. Shiaoyi, Thermograms of Energetic Materials, Peiging China, (2002) 154.
5 J.-S. Lee, C.-K. Hsu, L.-K. Lin and C.-W. Huang, J. Therm. Anal. Cal., 56 (1999) 223.
6 J.-S. Lee, Thermochim. Acta, 392–393 (2002) 147.
7 B. Berger, E. L. Charely, J. J. Rooney and S. B. Warrington, Thermochim. Acta, 269/270 (1995) 639.
8 A. Marotta and A. Buri, Thermochim. Acta, 25 (1977) 150.
9 I. J. Dayley, S. Y. Ho and V. Nanut, Propell. Explo. Pyrot., 22 (1997) 296.
10 J.-S. Lee, Thermochim. Acta, 292–293 (2002) 147.
11 E. L. M. Krabbendam-LaHaye, W. P. C. de Klerk and R. E. Krämer, J. Therm. Anal. Cal., 80 (2005) 495.
12 K. Sikder, J. Therm. Anal. Cal., 79 (2005) 631.
13 B. Roduit, Ch. Borgeat, B. Berger, P. Folly, H. Andres, U. Schädeli and B.Vogelsanger, J. Therm. Anal. Cal., 85 (2006) 195.
14 D.-J. Peng, C.-M. Chang and M. Chiu, J. Therm. Anal. Cal., 83 (2006) 657.
15 J.-S. Lee and K.-S. Jaw, J. Therm. Anal. Cal., 85 (2006) 463.
16 A. Myburgh, J. Therm. Anal. Cal., 85 (2006) 135.
17 P. R. Underlill and M. F. Bardon, Propell. Explo. Pyrot., 23 (1998) 43.

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