Research paper

Thermal characterization of pyrotechnic flash compositions

S. P. Sivapirakasam*, M. Surianarayanan**†, and F.Chandrasekaran**

*Department of Mechanical Engineering, National Institute of Technology, Tiruchirappalli – 620 015, India.

**Cell for Industrial Safety & Risk Analysis, Chemical Engineering Department, Central Leather Research Institute, (Council of Scientific & Industrial Research), Adyar, Chennai – 600 020, India.

†Corresponding address : msuri1@vsnl.com

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Abstract

Thermal characterization of pyrotechnic flash compositions by DSC showed multiple exotherms around 170°C and 350°C. The flash composition based upon potassium perchlorate/sulphur/aluminum and barium nitrate/sulphur/aluminum was found to be hazardous due to its secondary exothermic reaction with high energy release. The pyrotechnic flash compositions consisting of aluminum as a fuel showed a good cracking characteristics compared to other fuels like magnesium or charcoal. In all the compositions studied, the variation of sulphur concentration in a mixture showed a significant influence in inducing an exothermic reaction. Hence, proper care should be taken in use of sulphur concentration in a mixture during manufacturing.

Keywords : fireworks, thermal hazards, DSC, flash composition, exothermic reaction

1. Introduction

Thermal characterization of pyrotechnic compositions is important for fixing operating limits for safe chemical manufacturing process, and reducing the devastating effects during processing[1]. Industrial level exothermic chemical reactions and thermally unstable chemical compounds continue to be the areas of active research. In pyrotechnic industry, inadequate knowledge on exothermic hazards and reactivity of the chemicals during processing has caused casualties and material loss[2].

Thermal analysis is a technique used to characterize the unstable nature of chemical compounds. It is done by measuring changes in their physical and chemical properties as a function of temperature, usually by heating at a uniform rate. Even though there are a few reported studies on thermal hazards of fireworks composition[3)–5)], attention has not been paid to study and compare the thermal stability of different pyrotechnic flash compositions. In this paper, thermal hazards of various pyrotechnic flash compositions with different oxidizer and fuel were studied using differential scanning calorimeter at different heating rates.

1.1 Chemistry of flash composition used in fireworks

The flash composition used in fireworks contains mainly oxidizer, igniter, and fuel. Commonly, one of these components potassium chlorate/potassium perchlorate/barium nitrate/potassium nitrate is used as an oxidizer in a flash composition whereas sulphur is used as the igniter due to its lower melting point (119°C) and aluminum/magnesium/charcoal as the fuel. When a cracker is ignited in the wick, sulphur melts on ignition. On melting, the atom's physical contact is increased[6]. It is more likely that the atoms with energies exceeding activation energy will be in contact and react. As the reaction rate increases, the energy production rate increases leading to thermal runaway even at a lower temperature and the cracker mixture to explode. To propagate maximum energy through high heat of reaction, and low ignition temperature, it is important that efficient energy transfer takes place from the reacting to pre−reacting material by conduction, radiation and convection. Therefore, a combination of the above mentioned factors facilitate ignition for cracking reactivity.

Table 1 Pyrotechnic flash compositions under thermal characterization study

Sl.No.	Type of flash compositions	Flash composition in wt.%
1)	Potassium perchlorate based composition	$KClO_4$=64 wt.%, Al=23 wt.%, S=13 wt.%
		$KClO_4$=50 wt.%, Al=23 wt.%, S=27 wt.%
2)	Barium nitrate based composition	$Ba(NO_3)_2$. =66 wt.%, Al=25 wt.%, S=9 wt.%
		$Ba(NO_3)_2$. =70 wt.%, Al=10 wt.%, S=20 wt.%
3)	Potassium nitrate based composition	KNO_3=50 wt.%, Al=30 wt.%, S=20 wt.%
		KNO_3=50 wt.%, C=25 wt.%, S=25 wt.%
		KNO_3=57 wt.%, Mg=32 wt.%, S=11 wt.%
4)	Strontium nitrate based composition	$Sr(NO_3)_2$=30 wt.%, Al=70 wt.%

2. Experimental

2.1 Materials and methods

The chemicals used for the preparation of the flash compositions were obtained from fireworks manufacturing company situated in the southern state of Tamilnadu, India. The purity and assay of the chemicals were : Potassium nitrate −91.6 wt.%, barium nitrate −92 wt.%, potassium perchlorate −93 wt.%, strontium nitrate −92 wt.% and sulphur −99.84 wt.% and aluminum −99.71 wt.%, magnesium −99 wt.% and charcoal −98 wt.%. The chemicals were passed through a 100−mesh brass sieve. The samples were stored in an airtight container and kept away from light and moisture. The different flash compositions used in this study were from the standard references[7)−9)] and it is shown in the Table 1.

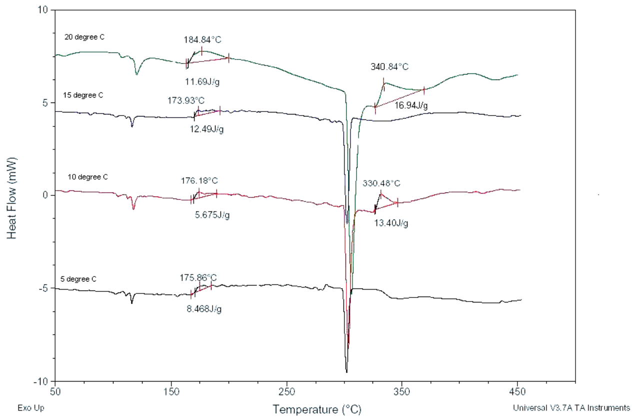

Fig. 1 DSC plots showing the influence of heating rates on thermal decompositions of a pyrotechnic flash composition ($KClO_4$=64 wt.%, Al=23 wt.%, S=13 wt.%)

2.2 Differential scanning calorimeter (DSC)

TA Instrument's, DSC module 2910 model was used for thermal stability studies for various pyrotechnic flash compositions. DSC consisted of sample chamber of 250 µl capacity. A small quantity, 2mg of the sample was taken in an aluminum pan. The pan was sealed with an aluminum lid and placed in the sample thermocouple of the DSC chamber. A supply of 100 µl of nitrogen gas was continuously purged in the DSC chamber. It was heated at a constant heating rate of 5, 10, 15, 20 K min^{-1} to an end temperature of around 450°C. An online PC continuously monitored the thermal changes and it plotted an online thermogram. From the thermogram the onset temperature, peak temperature and heat of reaction were evaluated for each flash composition.

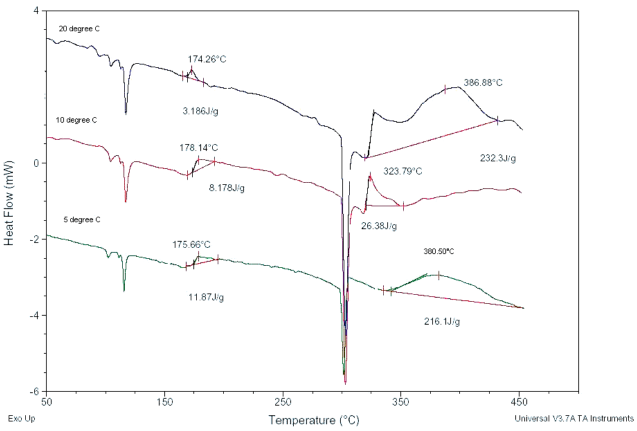

Fig. 2 DSC plots showing the influence of heating rates on thermal Decompositions of a pyrotechnic flash composition ($KClO_4$=50 wt.%, Al=23 wt.%, S=27 wt.%)

3. Results and discussion

3.1 Effect of potassium perchlorate flash composition on thermal decomposition at varying heating rates

The DSC plots (Figs. 1 and 2) show the influence of heating rate on the thermal decomposition of pyrotechnic flash compositions consisting of $KClO_4$=64 wt.%, Al=23 wt.%, S=13 wt.% and $KClO_4$=50 wt.%, Al=23 wt.%, S=27 wt.% respectively. On varying the heating rates the first exotherm was generally found to onset around 180°C. The exotherm was found to be more prominent at the higher heating rates than at the lower heating rates. Pure potassium perchlorate had an endothermic peak at around 300°C corresponding to a rhombic—cubic transition[10)]. In some cases immediately after the endotherm at the higher heating rates a secondary exotherm was observed. The occurrence of the secondary exotherm was more prominent in the DSC plot of Fig. 2 than Fig. 1. This was due to increase in sulphur concentration in a pyrotechnic mixture. Table 2 shows the DSC thermal data for the potassium perchlorate based flash compositions.

Table 2 DSC thermal data for potassium perchlorate based flash composition

Flash composition	Heating rates °C	First exotherm			Second exotherm		
		Onset temperature °C	Peak temperature °C	ΔH J/g	Onset temperature °C	Peak temperature °C	ΔH J/g
$KClO_4$=64wt.%, Al=23wt.%, S=13wt.%	5	172	175.86	8.468	—		
	10	171.96	176.18	5.675	325.70	330.48	13.40
	15	170.57	173.93	12.49	—		
	20	173.25	184.84	11.69	330.1	340.84	16.94
$KClO_4$=50wt.%, Al=23wt.%, S=27wt.%	5	171.74	175.66	11.87	339.98	380.50	216.1
	10	173.20	178.14	8.178	320.03	323.79	23.38
	20	170.47	174.26	3.186	322.10	368.88	232.3

3.2 Effect of barium nitrate based flash composition on thermal decomposition at varying heating rates

The DSC plots of pyrotechnic flash compositions consisting of $Ba(NO_3)_2$ =66 wt.%, Al=25 wt.%, S=9wt.% and $Ba(NO_3)_2$ =70 wt.%, Al=10 wt.%, S=20 wt.% at varying heating rates are shown in the Figs. 3 and 4 respectively. Table 3 shows the DSC thermal data for the barium nitrate based flash compositions. The trend of the curve was almost similar for both the flash compositions. A first endotherm occurred around 119°C was due to the melting of sulphur in a composition. On varying heating rates, the first exotherm was found to onset around 175°C. The exotherm was found to be more prominent at the higher heating rates than at the lower heating rates. The secondary exotherm was found to be around 350°C. The secondary exotherm was found to be more prominent compared with the first exotherm as well as at the higher heating rates. The secondary exotherm obtained in the flash composition ($Ba(NO_3)_2$ =66 wt.%, Al=25 wt.%, S=9wt.%) was less prominent than the other composition ($Ba(NO_3)_2$ =70 wt.%, Al=10 wt.%, S=20 wt.%). This proves the fact that increase in the composition of sulphur plays a vital role in influencing higher energy release during thermal decomposition.

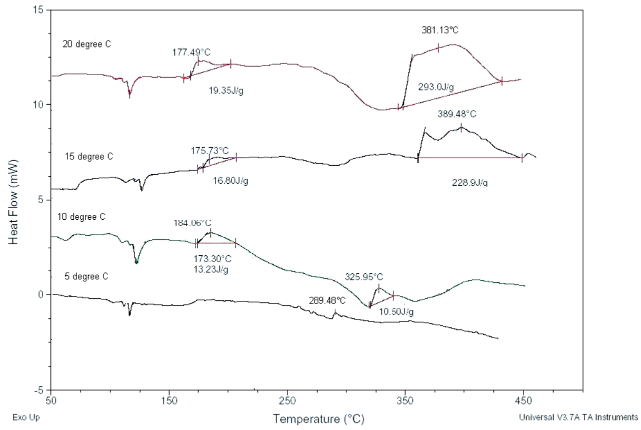

Fig. 4 DSC plots showing the influence of heating rates on thermal Decompositions of a pyrotechnic flash composition ($Ba(NO_3)_2$ =70 wt.%, Al=10 wt.%, S=20 wt.%)

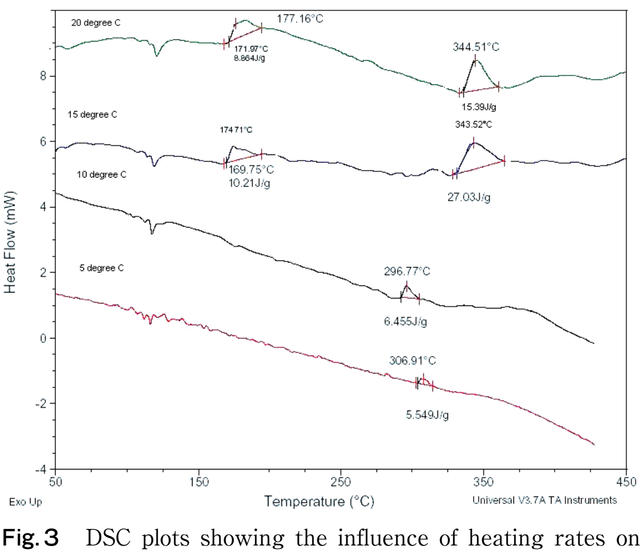

Fig. 3 DSC plots showing the influence of heating rates on thermal Decompositions of a pyrotechnic flash composition ($Ba(NO_3)_2$ =66 wt.%, Al=25 wt.%, S=9wt.%)

3.3 Effect of potassium nitrate based flash composition on thermal decomposition at varying heating rates

The DSC plot shows (Fig. 5) the influence of heating rate on the thermal decomposition of a pyrotechnic flash composition consisting of KNO_3=50 wt.%, Al=30 wt.%, S=20 wt.%. The first endotherm was found at 119°C, which was due to the melting of sulphur. At around 170°C, there was a first exotherm. A prominent secondary exotherm appeared only at higher heating rates (15°C, 20°C). This provides evidence that the flash composition is vulnerable at higher heating rates than at lower heating rates.

Fig. 6 shows the DSC plot at various heating rate on the thermal decomposition of a black powder consisting of KNO_3=50 wt.%, C=25 wt.%, S=25 wt.%. On all heating rates there was an endotherm set around 120°C. This endotherm was due to the melting of sulfur. At the higher heating rates (10, 15, 20°C/min) an exotherm was found around 320°C. At the lower heating rates i.e. at 5°C/min a sharp exotherm was found around 430°C. This explicates the fact that the pyrotechnic composition of KNO_3 : C : S ; in the ratio of 50 : 25 : 25 was extremely vulnerable at lower heating rates.

Table 3 DSC thermal data for barium nitrate based flash composition

Flash composition	Heating rates °C	First exotherm			Second exotherm		
		Onset temperature °C	Peak temperature °C	ΔH J/g	Onset temperature °C	Peak temperature °C	ΔH
$Ba(NO_3)_2$ =66wt.%, Al=25wt.%, S=9wt.%	5	–	–	–	302.97	306.91	5.549
	10	–	–	–	293.03	296.77	6.455
	15	169.75	174.71	10.21	331.83	343.52	27.03
	20	171.97	177.16	8.864	335.90	344.51	15.39
$Ba(NO_3)_2$ =70wt.%, Al=10wt.%, S=20wt.%	5	–	–	–	–	–	–
	10	173.30	184.06	13.23	319.30	325.95	10.50
	15	170.70	175.73	16.80	352.83	389.48	228.9
	15	171.55	177.49	19.35	351.12	381.13	293

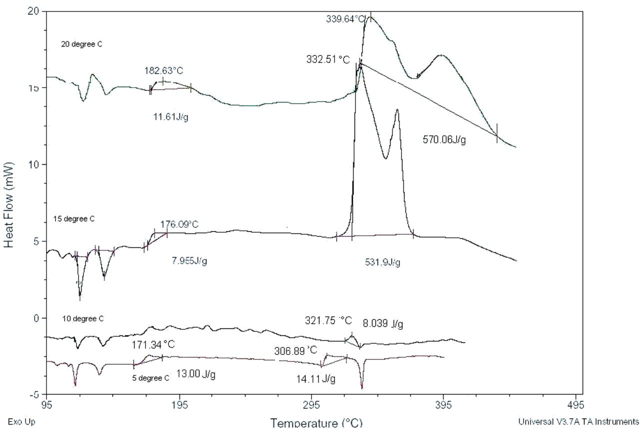

Fig. 5 DSC plots showing the influence of heating rates on thermal decompositions of a pyrotechnic flash composition (KNO_3=50wt.%, Al=30wt.%, S=20wt.%)

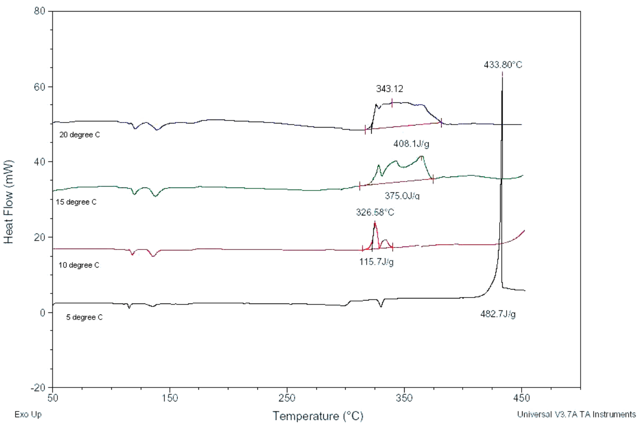

Fig. 6 DSC plots showing the influence of heating rates on thermal decompositions of a black powder (KNO_3=50 wt.%, C=25 wt.%, S=25 wt.%)

Figure 7 shows the thermal decomposition of the pyrotechnic flash composition consisting of KNO_3=57 wt.%, Mg =32 wt.%, S=11 wt.% at varying heating rates. The first endotherm was found to occur at 119°C, which was due to the melting of sulphur. The onset temperature of first exotherm spotted at 170°C ; the exotherm was prominent at higher rates than at the lower heating rates. The endotherm observed at 331°C was due to the melting of potassium nitrate. From the plot, it is apparent that the exothermic peak is not sharp and energy released during reaction would not allow the mixture to explode. Hence, this composition is not suitable to be used as a flash composition mixture. Table 4 shows the DSC thermal data for the potassium nitrate based flash compositions.

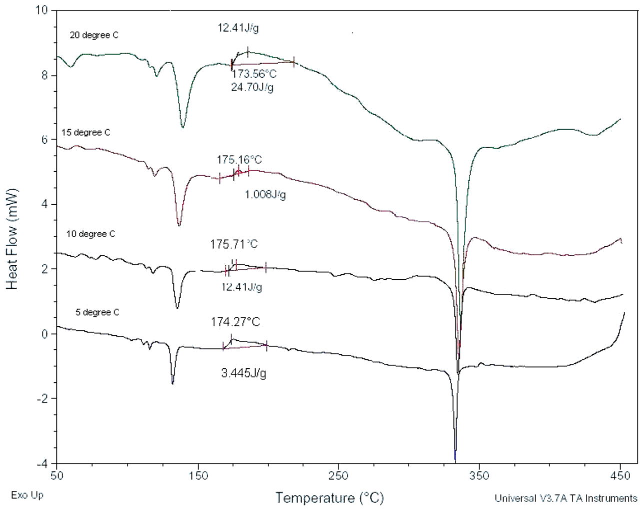

Fig. 7 DSC plots showing the influence of heating rates on thermal decompositions of a pyrotechnic flash composition (KNO_3=57wt.%, Mg=32wt.%, S=11wt.%)

3.4 Effect of strontium nitrate based composition flash composition on thermal decomposition at varying heating rates

The DSC plot (Fig. 8) shows the influence of heating rate on the thermal decomposition of a pyrotechnic flash composition consisting of $Sr(NO_3)_2$=30 wt.%, Al=70 wt.% and corresponding thermal data is shown in Table 5. On varying the heating rates the first exotherm was generally found to onset around 180°C. The exotherm was found to be more prominent at the higher heating rates than at the lower heating rates. However, this composition may not be used as a flash composition as the energy released during exothermic reaction is less.

Table 4 DSC thermal data for potassium nitrate based flash composition

Flash composition	Heating rates °C	First exotherm			Second Exotherm		
		Onset temperature °C	Peak temperature °C	ΔH J/g	Onset temperature °C	Peak temperature °C	ΔH
KNO_3=50wt.%, Al=20wt.%, S=30wt.%	5	166.74	171.34	13.00	303.88	306.89	14.11
	10	–	–		321.32	321.75	8.039
	15	170.70	176.09	13.00	325.65	332.51	531.9
	20	173.50	182.63	11.61	330.58	339.64	570.0
KNO_3=50wt.%, C=25wt.%, S=25wt.%	5	425	433.80	482.7	–	–	–
	10	324.27	326.58	115.7	–	–	–
	15	323.61	364.75	375	–	–	–
	20	325.52	343.12	408.1	–	–	–
KNO_3=57wt.%, Mg=32wt.%, S=11wt.%	5	171.25	174.27	3.445	–	–	–
	10	170.75	175.71	12.41	–	–	–
	15	171.98	175.16	1.008	–	–	–
	20	173.56	184.77	24.70	–	–	–

Table 5 DSC thermal data for strontium nitrate based flash composition

Flash composition	Heating rates °C	First exotherm			Second exotherm		
		Onset temperature °C	Peak temperature °C	ΔH J/g	Onset temperature °C	Peak temperature °C	ΔH
$Sr(NO_3)_2$=30wt%, Al=70wt.%	5	162.71	170.79	8.591	–	–	–
	10	160.26	172.11	6.916	–	–	–
	15	161.09	173.32	5.115	–	–	–
	20	178.77	178.77	14.43	–	–	–

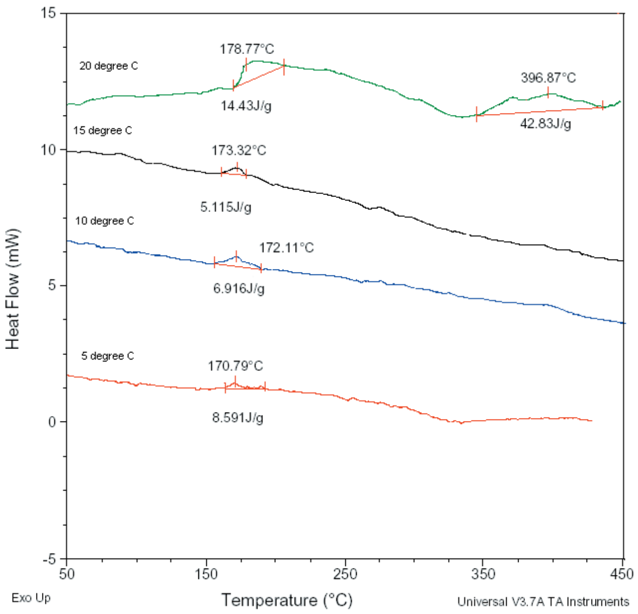

Fig. 8 DSC plots showing the influence of heating rates on thermal decompositions of a pyrotechnic flash composition ($Sr(NO_3)_2$=30 wt.%, Al=70 wt.%)

4. Process safety during processing of flash composition

Experimental investigation showed that the pyrotechnic flash compositions based on potassium perchlorate/sulphur/aluminum and barium nitrate/sulphur/aluminum was highly vulnerable and hazardous due to its secondary exothermic reaction with high energy release. This trend should be cautiously viewed in considering the safety aspects. All the mixtures studied were found to onset at a temperature around 170°C.However, the reactive potential under adiabatic conditions may be much more severe and earlier onset of exothermic activity is possible[11]. Therefore, these flash compositions have to be studied by Accelerating rate calorimeter (ARC) to understand the decomposition mechanism and the vigorous nature of chemical reaction. The pyrotechnic flash compositions based on the barium nitrate/sulphur/aluminum and potassium nitrate/sulphur/aluminum showed a hazardous property only at the higher heating rates.

The pyrotechnic flash compositions consisting of aluminum as a fuel showed a good cracking characteristics compared to other fuels like magnesium or charcoal. In all the compositions studied, the variation of sulphur concentration in a mixture showed a significant influence in inducing an exothermic reaction. Hence, proper care is necessary in use of sulphur and its concentration levels in a mixture during manufacturing as it is prone to initiate early exothermic activity.

5. Conclusion

DSC experiments for various types of flash compositions show that the mixtures undergo thermal decomposition with exothermic activity. In most of the compositions the secondary exotherms are prominent at higher heating rates. Generally the first onset is set around 160−170°C for all the compositions except the black powder. Hence it is difficult to identify an ideal flash composition which is safe both to manufacturer and user. However studies on mechanical sensitiveness and noise level measurement of flash composition can be further helpful in addressing safety related issues.

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References

1) T. Shimizu, 'Fireworks : The Art Science and Technique', Maruzen, Tokyo, Japan, (1981).
2) P.D Lightfoot, R.C. Fruchard, A.M. Turcotte and Q.S.M. Kwok, 'Thermal techniques used in the hazard evaluation of pyrotechnics', Journal of Pyrotechnics, Vol.14, pp.15−24, (2001).
3) S.P. Sivaprakasam, M. Surianarayanan, F. chandrasekran, and G. Swaminathan, Thermal hazards of cracker mixture using DSC, Journal of thermal Analysis and Calorimetry, No.78, p 799, (2004).
4) D. Chapman, R.K. Wharton, and G.E. Williamson, "Studies for the thermal stability and sensitiveness of sulfur/chlorate mixture Part I—Introduction", Journal of Pyrotechnics, No.6, p 30, (1997).
5) P.G. Laye and E.L. Charsley , 'Thermal analysis of pyrotechnics', Thermochimica Acta, Vol.120, pp.325−346, (1987).
6) W. D. Smith, "Introductory chemistry for pyrotechnics, Part 1 : Atoms, molecules, and their interactions", Journal of Pyrotechnics, No.1,p 12−25 (1994).
7) U. Krone and H. Treumann, 'Pyrotechnic flash compositions', Propellants, Explosives, Pyrotechnics, Vol.15, pp.115−120. (1990).
8) R.R. Lancaster, 'Fireworks principles and practice', Chemical Publishing Co., New York, p.25. (1972).
9) H. Ellern, 'Modern pyrotechnics', Chemical Publishing Co., New York, p.272. (1961).
10) Pourmatazavi et. al. 'Thermal behavior aluminum powder and potassium perchlorate by DTA and TGA', Thermochemica Acta. (2006)
11) S.P. Sivapirakasam, M. Surianarayanan. and G. Vijayaraghavan, 'Thermal characterization and kinetic modeling of pyrotechnic flash composition under adiabatic conditions', Journal of Pyrotechnics, 23, 6, (2006).