Hazard Assessment and Effect of Nano-Sized Oxidizer on Sound Level Analysis of Firecrackers

T. L.Thanulingam,[a] A. Jeya Rajendran,[b] P. Karlmarx,[c] K. Subramanian[c] and A. Azhagurajan[c]

[a] Fireworks Research and Development Centre, Petroleum and Explosives Safety Organisation, Anayoor village, Sivakasi - 626124, India. Email: tlthanulingam@yahoo.co.in

[b] Department of Chemistry, Loyola College, Nungambakkam, Chennai-600034, India
Email: jeyarajendran@yahoo.com

[c] Department of Mechanical Engineering, MEPCO Schlenk Engineering College, Sivakasi-626005, India

Abstract: *Nano-sized sulphur and oxidizers were synthesized by the ball mill method and the size was determined using a particle size analyzer. Pyrotechnic mixtures of compositions using five different oxidizers: potassium nitrate (KNO_3), potassium perchlorate ($KClO_4$), barium nitrate ($Ba(NO_3)_2$), strontium nitrate ($Sr(NO_3)_2$) and bismuth oxide (Bi_2O_3), in different particle sizes, mixed with sulphur (S), aluminium (Al) and boric acid (H_3BO_3), were used to produce sound producing cake-bomb firecrackers for analysis. A bulk density of 0.24–0.68 g cm^{-3} was maintained for homogeneity of the mixture. The sound level from newly formulated sound producing firecrackers (cake-bombs) showed a linear relationship with the weight of the mixture taken. Decreasing the particle size from micro to nano improves the efficiency of firecrackers using the oxidizers, KNO_3, $KClO_4$ but not for $Ba(NO_3)_2$, $Sr(NO_3)_2$, or Bi_2O_3. The analysis of safety characteristic data of thermal and mechanical sensitiveness indicates that the pyrotechnic mixture using the oxidizer $KClO_4$ is highly sensitive to friction and impact. The limiting impact energy (LIE) of pyrotechnic compositions falls in the range of 2.55–4.51 J. LIE of nano materials was less compared to micro materials indicating that as the particle size decreases, the mixture is prone to hazards from impact. Thermal analysis indicates a high temperature for self propagating decomposition making the mixture thermally stable at room temperature.*

Keywords: *Sound level, pyrotechnic mixture, impact sensitiveness, friction sensitiveness, flash composition, firecrackers.*

Introduction

'Fireworks' are a type of pyrotechnic device used for entertainment. The chemicals employed and their compositions vary depending on the type of fireworks being produced. Fireworks are made of an oxidizer, a fuel, and optionally, a colour enhancing chemical and a binder. The choice of fuels and oxidizers can significantly affect activation energy, heat of reaction and the efficiency of energy feedback.[1] The selection of fuel and oxidizer has the potential for having a major influence on the efficiency of the pyrotechnic mixture. Activation energy, the amount of energy required for an oxidizer to make its oxygen available to react with the fuel, depends on the nature of the oxidizer. Some oxidizers require input of a large amount of energy, while others actually produce energy in the process of releasing their oxygen. There is always an optimum fuel to oxidizer ratio, which produces the fastest burning rate. This corresponds to the situation where the reaction will be essentially complete with little fuel or oxidizer remaining after the reaction.[2] When the fuel to oxidiser ratio deviates from the optimum value, burn rate is reduced. The burn rate

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continues to fall as the deviation from optimum increases. During the process of manufacturing fireworks, chemicals are initially mixed to produce a reasonably homogeneous mixture. During these operations impact, friction, spark and heat stimuli may occur and, under certain conditions, one or more stimuli may be enough to cause ignition of the compositions. The sensitiveness of a pyrotechnic mixture depends on, amongst other things, the type, compositions, purity and moisture content of the chemicals used.[3] The results from burning a particular pyrotechnic composition depend on various factors. Chemicals used as additives even in small quantities to improve their mechanical properties can alter the combustion process and ignition temperature to lower temperature. The effectiveness of firecrackers depends not only on the compositions of mixtures, but also on factors such as particle size and shape, choice of fuel and oxidizers, fuel to oxidizer ratio, degree of mixing, moisture content, physical form, packing density, presence of additives, local pressure, degree of confinement, degree of consolidation, crystal effects and purity of the chemicals.[2] The present study assesses the impact and friction sensitiveness of the optimized pyrotechnic mixture for safety considerations and studies the sound level produced from the fireworks by changing the oxidizers and their particle size.

Experimental

Chemicals and materials

The chemicals used for the preparation of the firecrackers were obtained from a firework manufacturing company. The purity and assay of the chemicals were potassium nitrate (KNO_3), potassium chlorate ($KClO_4$), strontium nitrate ($Sr(NO_3)_2$), barium nitrate ($Ba(NO_3)_2$) and bismuth trioxide (Bi_2O_3) – 97.6%, sulphur (S) – 99.9%, aluminium (Al) – 99.8% and boric acid (H_3BO_3) – 99% of micron-size and of nano-size. The chemicals used in making fireworks are aluminium powders of grade 999 (200 mesh – 75 microns), KNO_3, $KClO_4$, $Sr(NO_3)_2$, $Ba(NO_3)_2$, and Bi_2O_3 of 120 mesh (125 microns), S of 100 mesh (150 microns) and H_3BO_3 of 100 mesh (150 microns) sizes. All these chemicals were sieved using a 100-mesh brass sieve. The samples were stored away from light and moisture till they were packed within the paper case of the firecracker unit

Figure 1. *Paper case and firecracker taken for analysis. Top: Inner paper case (large); bottom: Firecracker (cake-bomb).*

(Figure 1). Kraft paper (brown) with 240 GSM (gram per square meter) thickness which was measured by a GSM meter was used for making the inner shells of the firecrackers. Jute string with gum, of length 130–260 cm, and thin foil papers (cello paper) were used for making firecrackers. Small size paper cases of 15 × 15 × 15 mm (3.375 cm^3) (Figure 1) were used to prepare cake-bomb firecrackers, similar to commercially available firecrackers.

Preparation of nano-size pyrotechnic mixture

The Fritsch, GmbH, 'Pulverisette 6' planetary monomill was used for preparing different particle sizes of oxidizers and fuels. 20 g of the material (oxidizer/fuels separately) was placed into a bowl with 100 ml of ethanol, and then 50 tungsten balls were placed in the bowl. The lid was closed and locked. Milling was carried out for 15 min at a speed of 300 rpm. After cooling the bowl for 5 min, milling was again done for 15 min. If the ethanol level became low, some more ethanol was added in order to make the powder in the colloidal state. After grinding for 2 hours the colloidal state powder was transferred to an air-tight container and it was kept safe. To separate the powders from ethanol the container was kept in the open atmosphere. The powder was collected after evaporating the ethanol.

Measurement of particle size

The particle size was measured using a 'Zetasizer Nano ZS particle size analyzer'. Hydrodynamic or aerodynamic particle size equals the diameter of the sphere that has the same drag coefficient as a given particle. There are several methods for measuring particle size. Some of them are based on light, ultrasound, or electric field, or gravity, or centrifugation. The complexity in defining particle size appears for particles with sizes below a micrometer. When the particle becomes small, the thickness of the interface layer becomes comparable with the particle size. As a result, the position of the particle surface becomes uncertain and practically polydisperse, which means that the particles in an ensemble have different sizes. The statistical distribution of particle size reflects the polydispersity (Figures 2–5). There is often a need for a certain average particle size for the ensemble of particles. The particle size is measured by taking 0.01 g of the powder in a glass plate and drying it. It is mixed with 50 ml of ethanol and it is sonicated for 2 min. The sonicator works in the frequency range 20 to 50 kHz and the amplitude is set at 31%. After sonication, the solution is poured into the cuvette of the particle size analyzer which is made of polymer to measure the particle size. The bulk packing density was maintained constant for a particular type of oxidizer in order to maintain the homogeneity of the mixture. As the particle size of micro-sized materials was kept the same, the bulk packing density was found to vary from oxidizer to oxidizer.

Firecrackers

Cake-bomb firecrackers were manufactured manually by experienced technicians of the firework manufacturing company for analysis. A flow chart

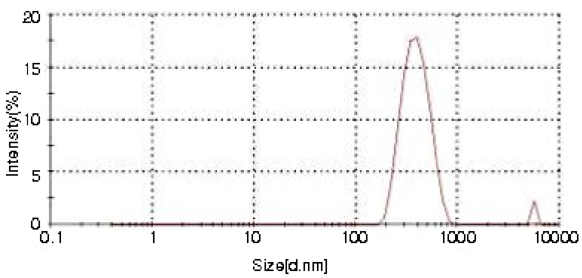

Figure 2. *Particle size distribution for KNO_3.*

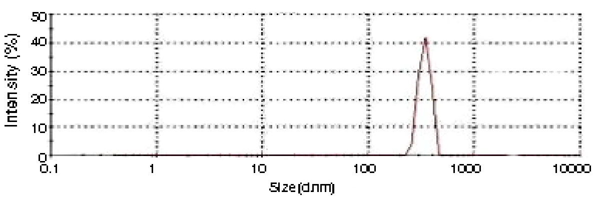

Figure 4. *Particle size distribution for sulphur.*

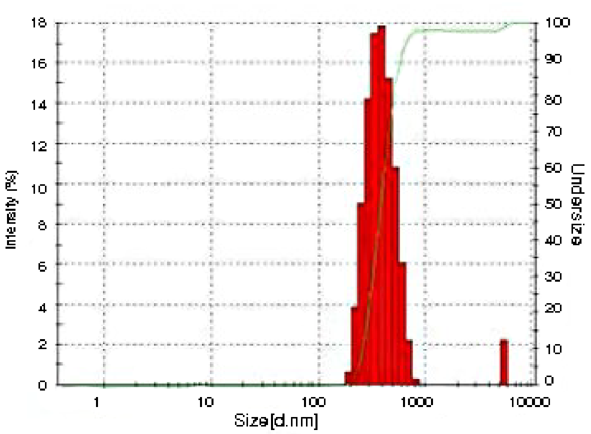

Figure 3. *Intensity peak statistics for KNO_3.*

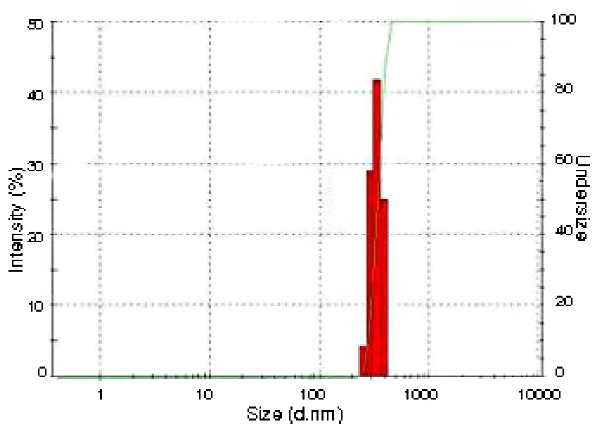

Figure 5. *Intensity peak statistics for sulphur.*

Table 1. *Flow chart for preparing cake-bomb.*

Weighing of chemicals
Mixing of chemicals
Filling of chemicals inside the shell
Closing of shell by tissue paper
Drying of shells
Jute wrapping over the shell
Drying of shells in sunlight
Fuse insertion into the shell
Drying of shell
Finished product

for preparing cake-bombs is given in Table 1. The chemical mixtures of $KNO_3/Al/S/H_3BO_3$, $KClO_4/Al/S/H_3BO_3$, $Sr(NO_3)_2/Al/S/H_3BO_3$, $Ba(NO_3)_2/Al/S/H_3BO_3$, $Bi_2O_3/Al/S/H_3BO_3$ in the molar ratio of 1.28/1.40/1.85/0.02 were sieved separately and mixed thoroughly in non-conducting surfaces like newspaper, rubber mat etc., by sieving through mesh No. 40 (425 microns), four to five times to get a homogeneous mixture of micro-size materials. This chemical mixture was filled inside the paper case of the firecracker unit. Thin foil papers (cello paper) were used to cover the paper case and it was sealed with gum and dried in atmospheric air. Jute string with gum of length 130–260 cm was wound round the paper case tightly and 3 windings were done, after which it was dried in sunlight for 2 to 3 hours (Figure 1). The fuse wire (100 mm, quick match) was inserted using a brass needle and kept in its place by charcoal powder. Coloured fancy papers were used to cover it for appearance and it was dried for about 24 hours in the sunlight to make the firecrackers ready for testing.

Instruments

Planetary ball mill

The planetary monomill was used for mixing and homogenisation of materials. The grinding mechanism of the planetary monomill is given in Figure 6 and the specifications of the ball mill are given in Table 2. The material was crushed and disintegrated in a grinding bowl by grinding balls. The grinding balls and the material in the grinding bowl were acted upon by the centrifugal forces due to the rotation of the grinding bowl about its own

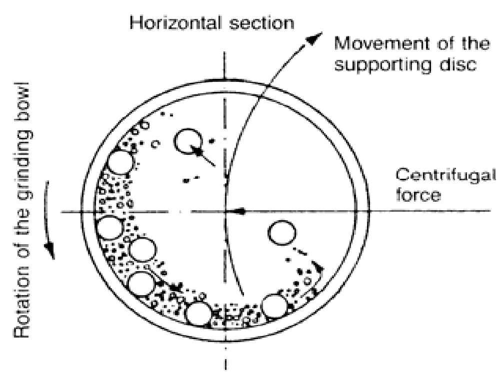

Figure 6. *Grinding mechanism.*

Table 2. *Specification of ball mill.*

Sample quantity	Up to 30 g
Voltage	240 volts AC
Weight	63 kg
Output size	0.001 to 1 micron
Operating principle	Impact
Speed	100-650 rpm
Grinding tools	Grinding bowls and grinding balls
Timer	Available selection – make
Grinding jar	Tungsten carbide – 250 ml
Grinding media	Tungsten carbide balls

axis and due to the rotation of the supporting disc. The grinding bowl and the supporting disc rotate in opposite directions, so that the centrifugal forces alternately act in the same and opposite directions. This results in, as a frictional effect, the grinding balls running along the inner wall of the grinding bowl, and as an impact effect, the balls impacting against the opposite wall of the grinding bowl. The bowl is made of tungsten carbide. The bowl consists of 50 balls and these balls are also made of tungsten carbide. The weight of each ball is 8 g and the bowl weight is 5 kg.

Sound level meter

The sound level test was carried out as per the rules of notification of PESO (Petroleum and Explosives Safety Organisation), formerly known as 'Dept. of Explosives', Govt. of India.[4] The noise level was measured by four sound level monitors using Model No.824L obtained from Larson & Davis, USA and the average values of the four readings were taken as sound level data.[5] Sound is usually measured in decibels (dB), a logarithmic unit used to describe a ratio of sound pressure [log (P_2/P_1) dB], or voltage or intensity. When it is used to give the sound level for a single sound rather than a ratio, a reference level is required. The most widely used sound level filter is the A scale, which roughly corresponds to the inverse of the 40 dB (at 1 kHz) equal-loudness curve. Using this filter, the sound level meter is thus less sensitive to very high and very low frequencies. Measurements made on this scale are expressed as dB(A). The C scale is practically linear over several octaves and is thus suitable for subjective measurements only for very high sound levels. Measurements made on this scale are expressed as dB(C). The sound level meters are capable of measuring the noise level in A, C, by flat weightings with slow, fast, impulse detectors. The measurements were taken at 1.2 m elevation from the level of bursting at 4 m distance. The meters were placed in four places such that the angle between them was 90^{o} and the average of these four values was taken as the sound level. A 5 m diameter hard concrete surface was used for carrying out the sound level test.[5] A microphone converted sound into electrical power and a decibel meter read out the sound power in watts or dB.

Impact sensitivity measurement

Impact sensitiveness of the pyrotechnic mixture was tested using the BAM method[6,7] by an impact sensitiveness tester. The design and principles of the equipment are similar to those of the drop fall hammer equipment of the BAM standards. The procedure followed in this study was based on the previously reported method.[8] The LIE of the sample was calculated using the formula:

$$\mathrm{LIE} = mgh$$

where m = mean of the drop weight (kg), g = acceleration due to gravity (9.81 m s^{-2}), h = height (m).

The validity of the results was tested by calibrating the machine with the LIE of standard substances and the results are given in Table 3. The impact energy measured was within acceptable limits of error (1–2%). Five runs were undertaken to check the reproducibility.

Friction sensitivity measurement

The friction sensitiveness was determined using a Friction Tester by the common test methods of BAM[4] and it corresponds to the UN Recommendations on the Transport of Dangerous Goods.[9] The friction test determines whether a pyrotechnic mixture possesses a danger of explosion or reaction when subjected to the effect of friction. When starting a test with materials, a weight was chosen approximately in the middle of the loading range. If two reactions were detected, then the load would be decreased. If no reactions occurred, then the load would be increased. Friction sensitiveness is a relative measurement reported in newtons (N), when ignition or explosion occurs only once in six repetitions.

Thermal analyser

Table 3. *Impact sensitiveness of standards to calibrate the impact sensitiveness apparatus.*

Substance	Reported impact energy (J)	Calculated impact energy (J)	Error (%)
Tetryl (dry)	4	4.05	2
Lead azide (dry)	2.5	2.6	2.5

Thermal analysis (TA), thermogravimetric (TG) and differential thermal analysis (DTA) were carried out using a Perkin-Elmer, Pyris diamond model thermal analyser with a rate of heating of 30 °C min^{-1} and a temperature range of a standard system of room temperature to 900 °C.

Differential scanning calorimetry

High temperature DSC analysis under ignition conditions was carried out using a Mettler Toledo, model DSC 821, with temperature range of −65 °C to 450 °C and heating rate of 10 °C min^{-1}.

Results and discussion

Sound level analysis

Factors affecting sound level

The sound level produced from firecrackers with different grades of Al, based on the particle size, was studied.[5] In this work, optimum conditions for making the firecracker cake-bomb were reported to produce a sound level of <125 dB(A)/145 dB(C) peak at 4 m distance, within the allowed level as prescribed by Govt. of India notification[4] by using aluminium of 999 (75 micron size) grade, an optimum quantity of pyrotechnic mixture of 1 g in an inner box of specified dimensions made up with kraft paper of GSM 240, bursting strength 2.2 kg cm^{-2}. The amount of the mixture that produced the sound level depends on the nature of the oxidizers (Table 4). Apart from all these factors, the sound level produced from the fireworks is greatly affected by the composition of the fireworks. In this paper, the sound level produced from the fireworks by varying five different oxidizers of micro and nano-sizes was studied.

Sound producing firecrackers (cake-bomb) were prepared from pyrotechnic mixtures of nano-size and micro-size using different oxidizers similar to commercial firecrackers. Sound level analysis was carried out and the data are given in Table 4. The effect of particle size in producing sound level varies from one oxidizer to another. If KNO_3 is used as oxidizer, decreasing the particle

Table 4. *Effect of oxidizer on sound level of firecrackers of nano-sized materials.*

Type of oxidizer	Wt. of chemicals/g	Size/ nm	Sound level		Size/ µm	Sound level	
			dB(A) peak	dB(C) peak		dB(A) peak	dB(C) peak
Potassium nitrate	0.25	397	121.1	144.6	250	106.6	131.5
	0.5		123.4	145.9		114.9	139.0
	0.75		130.3	152.9		122.0	144.4
	1.0		131.3	154.0		124.0	146.8
Strontium nitrate	0.25	147	Red flash		250	108.7	130.9
	0.5		Red flash			120.7	143.5
	0.75		Red flash			124.1	146.4
	1.0		Red flash			125.3	148.1
Potassium perchlorate	0.25	320	130.0	152.5	250	127.1	149.9
	0.5		131.8	154.5		130.3	152.7
	0.75		132.8	155.1		132.8	155.4
	1.0		134.2	156.2		134.4	156.5
Barium nitrate	0.25	122	Green flash	124.5	250	Green flash	Green flash
	0.5		101.5			Green flash	Green flash
	0.75		Green flash			Green flash	Green flash
	1.0		Green flash			Green flash	Green flash
Bismuth trioxide	0.25	461	No flash & sound	No flash & sound	250	No flash & sound	No flash & sound
	0.5						
	0.75						
	1.0						

*Inner box dimension:15 × 15 × 15 mm^3 3.375 cm^3); jute length 130 cm, winding: 3ply, GSM 240 g m^{-2}, bursting strength 2.2 kg cm^{-2}. Oxidizer/Al/S/H_3BO_3 (mole 1.28/1.40/1.85/0.02).

size from micro- to nano-sized will increase the effectiveness of the pyrotechnic mixture in producing sound. If the particles are nano-sized, 0.5 g of pyrotechnic mixture is sufficient to produce the optimum sound level whereas the same sound level is produced only by using 1 g of micro-sized pyrotechnic mixture (Table 4). It is expected that as the particle size decreases, the pyrotechnic mixture is effective in producing sound. The particle size effect can be considered to be the result of reducing the activation energy, because smaller particles require less energy to be heated to the ignition temperature.[2] Only atoms on the surface of particles are available to react, and as the particle size is reduced, the fraction of atoms on the surface increases.

If $KClO_4$ is used as oxidizer, the micro-sized particles produced sound effectively compared to nano-sized particles up to 0.5 g of pyrotechnic mixture (Table 4 and Figure 7) and on further increasing the amount of the mixture, nano-sized pyrotechnic mixture produced sound effectively. In the case of $Sr(NO_3)_2$ as oxidizer, firecrackers using the nano-sized pyrotechnic mixture produce no sound and they produce a red colour flash whereas the micro-sized firecrackers produce sound. In the case of $Ba(NO_3)_2$ as oxidizer, firecrackers using both nano- and micro-sized pyrotechnic mixtures produce no sound but produce a green flash.

Firecrackers using Bi_2O_3 in micro- and nano-sized produce neither flash nor sound. Even though oxygen is present, oxides are somewhat inert and the activation energy is not reached to initiate the reaction of oxidizers to release oxygen. Alkali nitrates and chlorate act as effective oxidizers compared to alkaline earth nitrates.

$KClO_4$ is a strong oxidizer at high temperatures and tends to cake more easily than KNO_3 and needs some anticaking agent. It becomes quite sensitive in contact with other chemicals and ignites very easily by friction.[1] Potassium nitrate alone does not explode even on a strong impact and acts as an oxidizing agent at high temperatures. If it is mixed with charcoal, Al or S, it decomposes and the amount of effective oxygen increases to the maximum value. Barium nitrate can also act as an oxidizer but it cakes to form a hard mass like a stone. The sound level produced from the firecrackers also varies depending on the oxidizer and their particle size which has not been reported earlier (Figures 7–9).

Mechanical sensitivity measurements

Friction sensitivity

The measurements of sensitiveness of the pyrotechnic mixtures $KNO_3/Al/S/H_3BO_3$, $KClO_4/Al/S/H_3BO_3$, $Sr(NO_3)_2/Al/S/H_3BO_3$, $Ba(NO_3)_2/Al/S/H_3BO_3$, and $Bi_2O_3/Al/S/H_3BO_3$, in the mole ratio 1.28/1.40/1.85/0.02 were carried out (Table 5) to indicate the ease of initiation by an accidental stimulus of the pyrotechnic mixture. The mechanical stress, like friction and impact sensitiveness of the pyrotechnic mixture, was

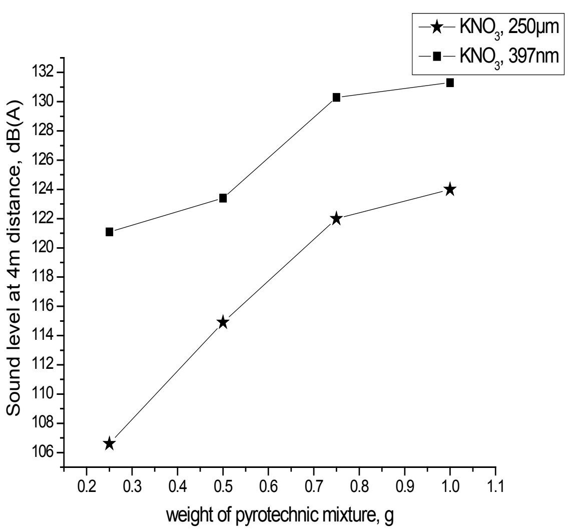

Figure 7. *Effect of the amount of pyrotechnic mixture on sound level.*

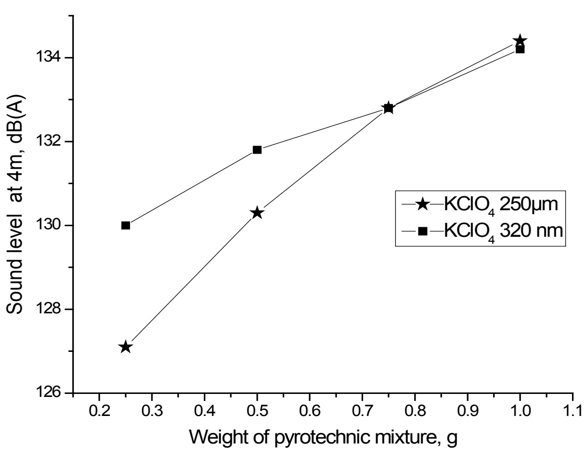

Figure 8. *Effect of the amount of pyrotechnic mixture on sound level.*

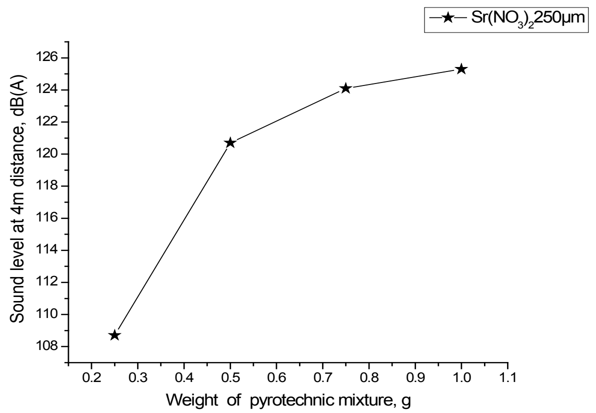

Figure 9. *Effect of the amount of pyrotechnic mixture on sound level.*

measured.[8] The friction sensitiveness was found to be >360 N for the pyrotechnic mixtures containing the oxidizers KNO_3, $Sr(NO_3)_2$, $Ba(NO_3)_2$ and Bi_2O_3 and 144 N for the mixture containing $KClO_4$ as oxidizer. High measurements indicate low friction sensitiveness and the pyrotechnic mixture is safer from accidental risk of mechanical stress.[8] Any material with a limiting load less than 80 N is considered too sensitive for transport of military pyrotechnics. In the case of manufacturing firecrackers, any material that produces a 'Threshold of Initiation' (TIL) greater than 184 N is deemed to be fit for transport.[9] The friction sensitiveness of the highly sensitive pyrotechnic mixture $KClO_4/S/Al(H_3BO_3)$ was found to be 144 N which is <184 N making it too sensitive for transport.

Impact sensitiveness

The impact sensitiveness of the pyrotechnic mixtures was measured in terms of the LIE (Table 5). The limiting impact energy was found to be 4.51, 2.75, 4.32, 4.12, and 3.53 J for the compositions of the firecrackers containing KNO_3, $KClO_4$, $Sr(NO_3)_2$, $Ba(NO_3)_2$ and Bi_2O_3 as oxidizers respectively along with $S/Al/H_3BO_3$ indicating that these compositions were sensitive to impact. If the limiting impact energy is low, the mixture is highly sensitive to impact. The pyrotechnic mixture with oxidizer $KClO_4$ is considered to be highly sensitive for friction and impact.

Thermal analysis

In order to understand the sensitivity of materials to heat and to determine the relative onset decomposition temperature, thermal analysis of ingredients, oxidisers/$S/Al/H_3BO_3$ was carried out (Figures 10, 11). The decomposition reaction of a pyrotechnic mixture containing different oxidizers follows the same mechanism and undergoes a two stage decomposition reaction occurring in the region of 200–300 °C and 500–600 °C. The first peak indicates the decomposition of S as SO_2 and the energy released is used up in initiating the explosion reaction of oxidizers. All the oxidizers are thermally stable for firecrackers at room temperature. The measurements of sensitiveness indicated that $KClO_4$ is highly sensitive to friction and impact compared to other oxidizers.

DSC Analysis

DSC analysis is used to determine quantitatively the thermodynamic parameters like ΔH and ignition temperature (Table 6). There is no overlap of the endothermic peaks and exothermic peaks. Below 437 °C, there is no exothermic peak and only endothermic peaks were observed.

DSC analysis of KNO_3 shows two endothermic peaks at 121 °C and 141 °C corresponding to the melting point of S and KNO_3, and one exothermic peak at 353 °C where maximum weight loss occurs

Table 5. *Sensitiveness of pyrotechnic mixtures.*

Pyrotechnic composition	Particle size		Bulk packing density/g cm^{-3}		Friction sensitiveness/N		Impact sensitiveness/J	
	(μm)	(nm)	micro	nano	micro	nano	micro	nano
*$KNO_3/Al/S/H_3BO_3$	250	397	0.34	0.24	>360	>360	4.51	3.14
*$KClO_4/Al/S/H_3BO_3$	250	320	0.41	0.31	144	168	2.75	2.55
*$Sr(NO_3)_2/Al/S/H_3BO_3$	250	147	0.43	0.30	> 360	> 360	4.32	3.92
*$Ba(NO_3)_2/Al/S/H_3BO_3$	250	122	0.47	0.27	> 360	> 360	4.12	3.33
*$Bi_2O_3/Al/S/H_3BO_3$	250	461	0.68	0.67	> 360	> 360	3.53	3.53

*(Oxidizer /$Al/S/H_3BO_3$ in the mole ratio 1.28/1.40/1.85/0.02).

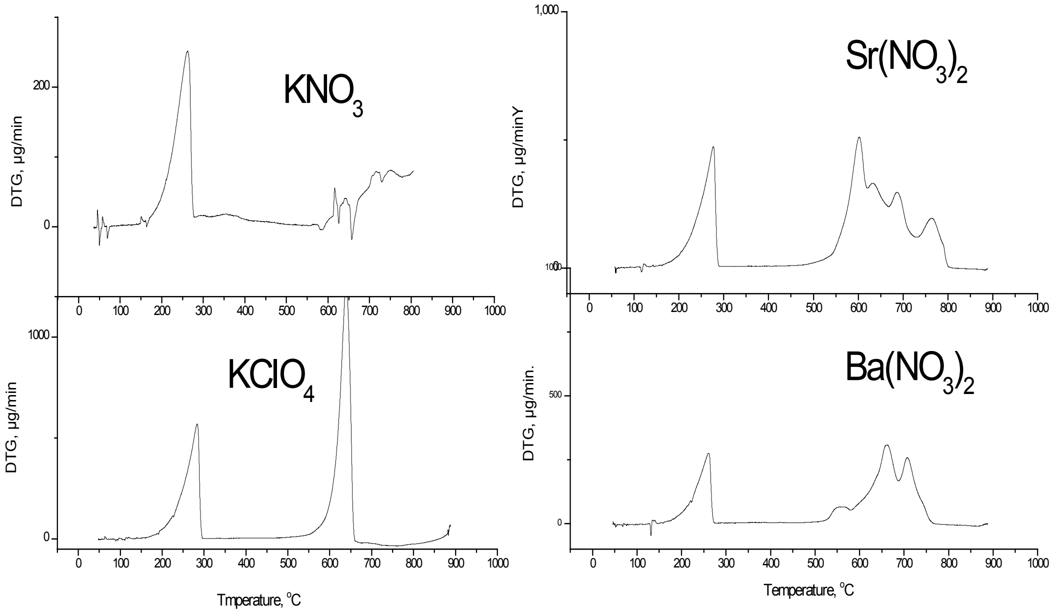

Figure 10. *DTG analysis of nano-sized pyrotechnic mixture, oxidisers/S/Al/H_3BO_3.*

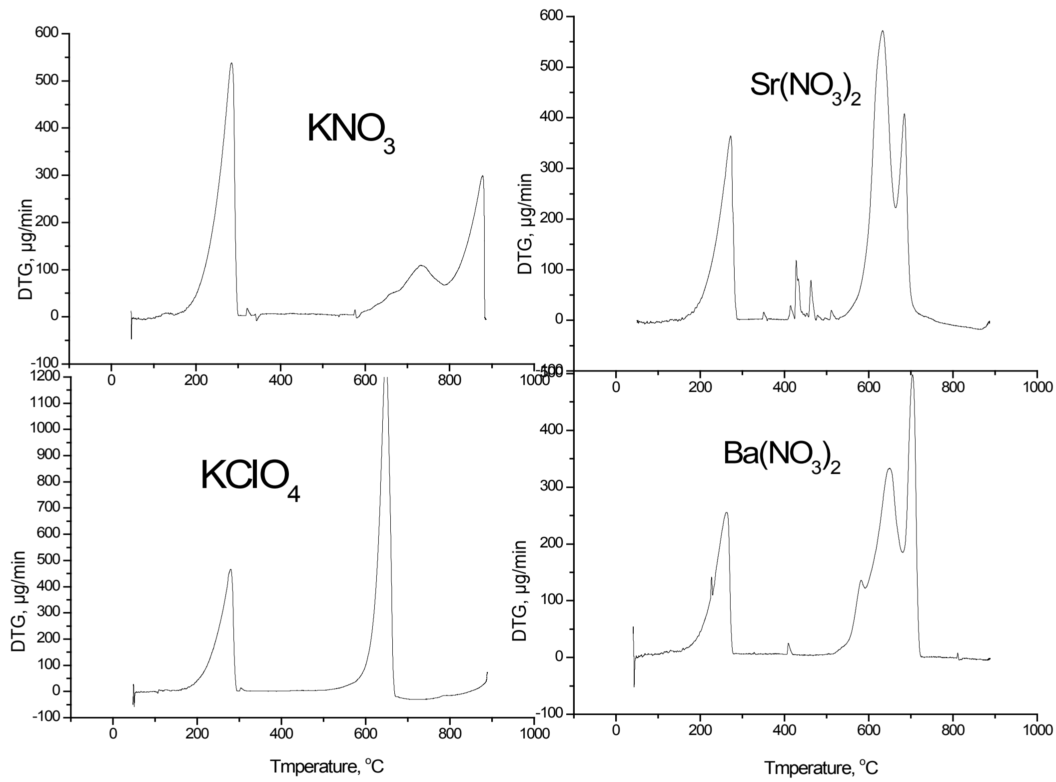

Figure 11. *DTG analysis of micro-sized pyrotechnic mixture, oxidisers/S/Al/H_3BO_3.*

Table 6 Thermal decomposition parameters by DSC analysis

No	Pyrotechnic composition	Particle size/nm	Onset/°C	Peak/°C	ΔH/J g^{-1}	Particle size/µm	Onset/°C	Peak/°C	ΔH/J g^{-1}
1	KNO_3/Al/S/ H_3BO_3	397	345.63	363.035	46.793	250	213.75	238.29	17.58
			504.15	58.94	9.19		250.16	258.81	9.10
							341.86	**354.90**	190.58
							446.13	508.53	42.68
2	$KClO_4$/ Al/S/H_3BO_3	147	235.03	248.78	9.30	250	361.73	372.43	16.59
			358.19	372.13	62.59		441.33	559.25	116.85
			446.72	552.57	74.86				
3	$Sr(NO_3)_2$/ Al/S/H_3BO_3	320	343.74	351.67	11.11	250	202.99	281.57	38.15
			412.89	549.04	436.93		335.11	346.78	18.02
4	$Ba(NO_3)_2$/ Al/S/H_3BO_3	122	353.98	366.65	31.80	250	337.41	349.49	19.86–102.9
			508.8	516.88	27.41		576.32	590.00	
5	Bi_2O_3/Al/S/ H_3BO_3	461	330.39	334.83	5.73	250	330.39	334.83	5.73
			479.35	485.20	19.46		479.35	485.20	19.46
			508.26	527.86	33.44		508.26	527.86	33.44

(Figures 12 and 13). There is no overlapping of exothermic and endothermic peaks. Pyrotechnic mixtures using nano- and micro-sized particles of oxidizers follow the same trend on thermal decomposition but the heat of reaction for nano-sized particles (47 J g^{-1}) is less than that of micro-sized particles (191 J g^{-1}) and the effect of sound level is inversely proportional to the heat of reaction, as the sound level produced by nano-sized particles is higher than that of micro-sized particles.

DSC analysis of $KClO_4$ (Figures 14 and 15) shows two endothermic peaks at 117 °C corresponding to the melting point of S and at 307 °C, a well defined solid–solid transition. This solid–solid transition peak makes $KClO_4$ one of the

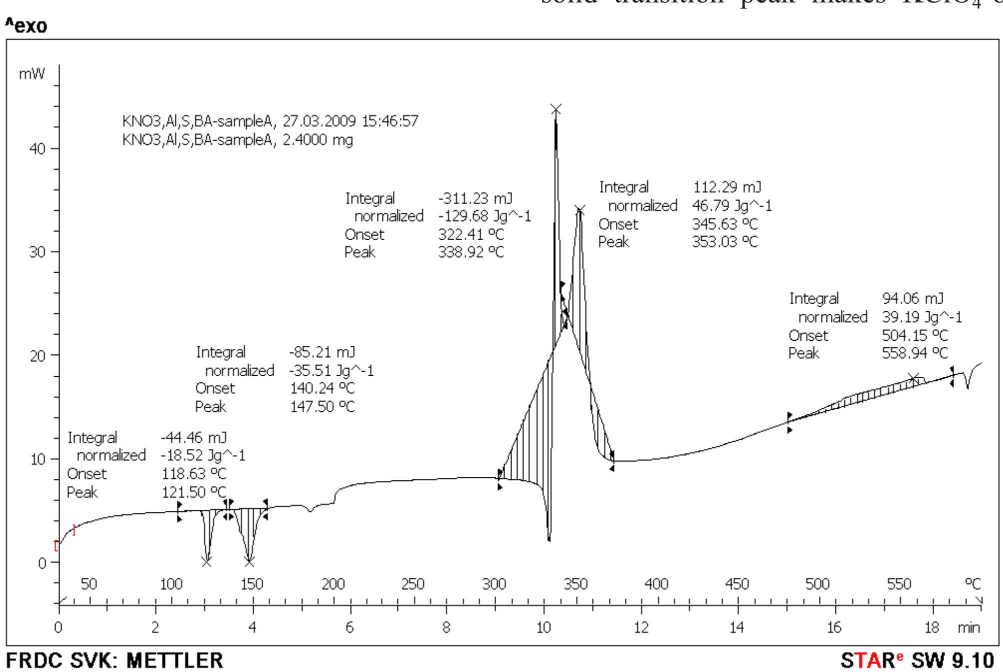

Figure 12. *DSC analysis of nano-sized pyrotechnic mixture, KNO_3/S/Al/H_3BO_3.*

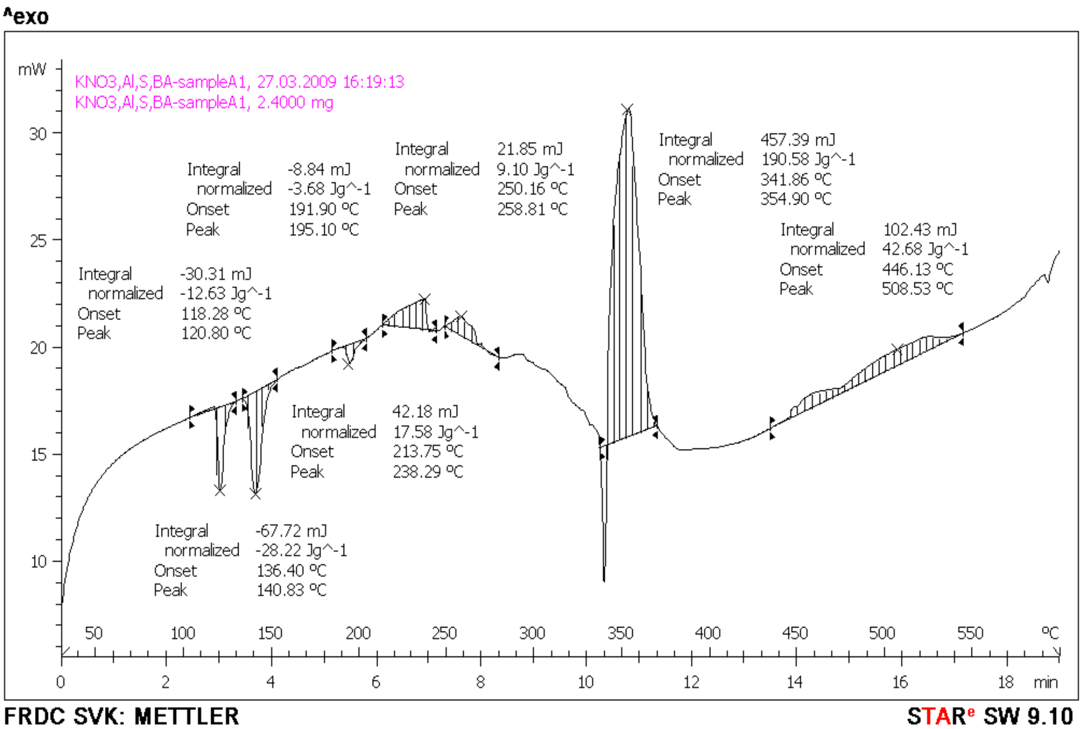

Figure 13. *DSC analysis of micro-sized pyrotechnic mixture, $KNO_3/S/Al/H_3BO_3$.*

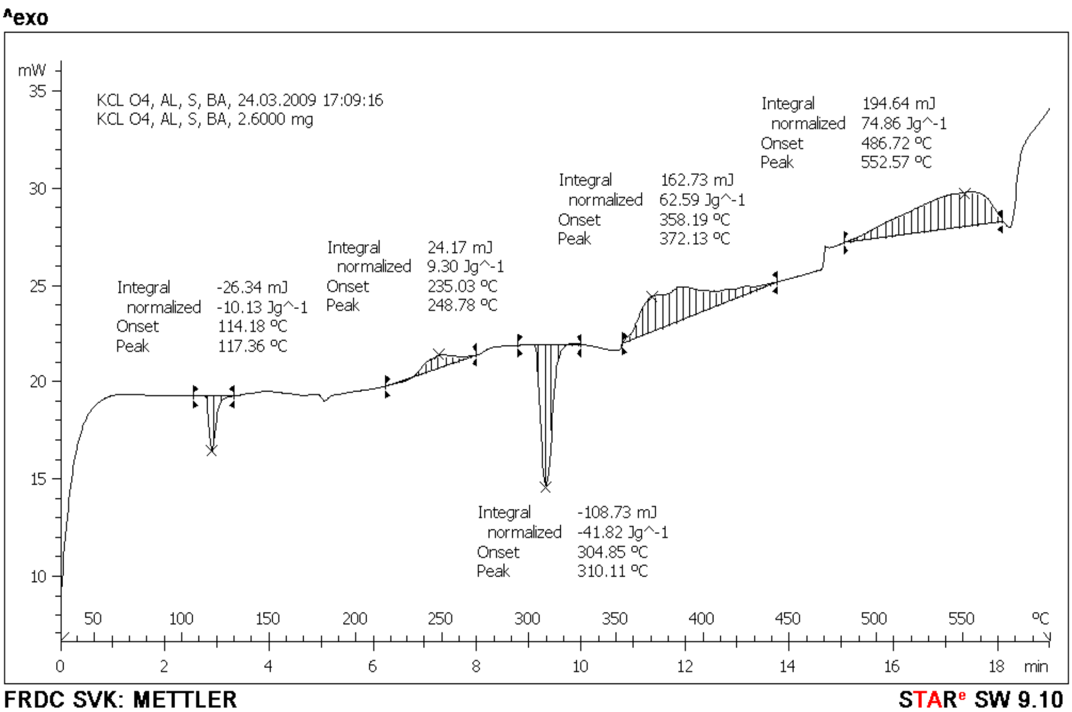

Figure 14. *DSC analysis of nano-sized pyrotechnic mixture, $KClO_4/S/Al/H_3BO_3$.*

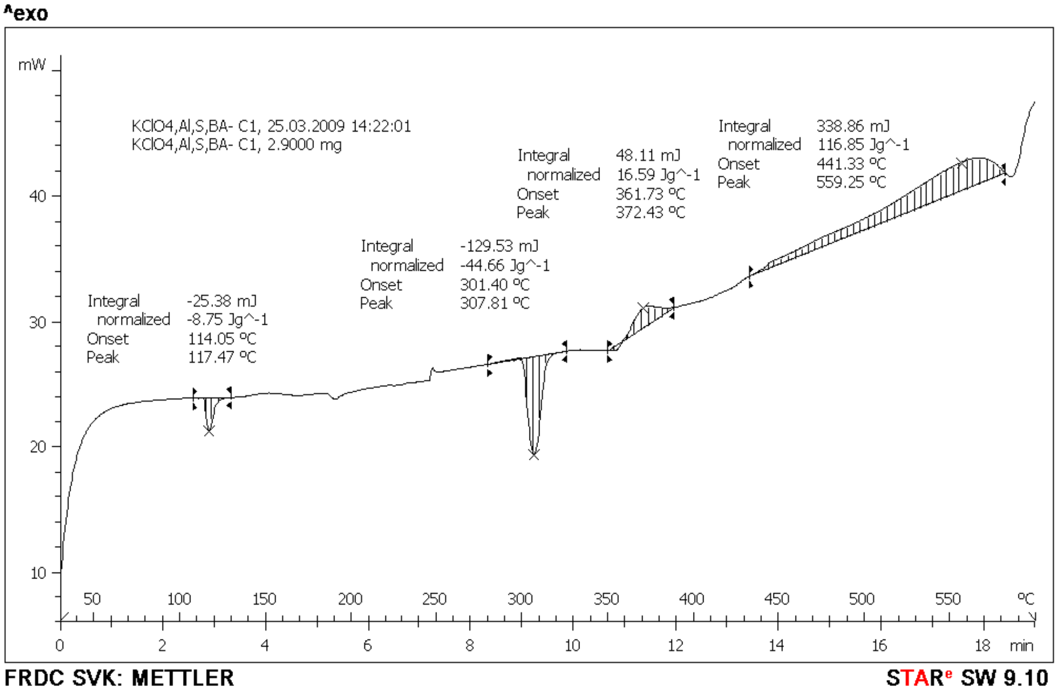

Figure 15. *DSC analysis of micro-sized pyrotechnic mixture, $KClO_4/S/Al/H_3BO_3$.*

Certified Reference Materials developed by the International Confederation for Thermal Analysis and Calorimetry (ICTAC) for the temperature calibration of DSC and DTA equipment[10] and the area of the solid–solid transition peak could be used as a semi-quantitative estimation of the amount of perchlorate present in a mixture. The exothermic peak at 249 °C represents the oxidation of sulphur into sulphur oxide. The exothermic peaks at 372 °C and 553 °C represent the decomposition where maximum weight loss occurs (Figure 14). The heat of reaction for nano-sized particles (136.9 J g^{-1}) is slightly greater than that of micro-sized particles (132 J g^{-1}) and the effect of sound level is inversely proportional to the heat of reaction, and there is not much difference in the sound level produced by nano-sized and micro-sized particles of $KClO_4$.

In the case of a pyrotechnic mixture with oxidizer $Sr(NO_3)_2$, two endothermic peaks at 117 °C due to the melting of S and at 351 °C correspond to the melting of $Sr(NO_3)_2$ (Figures 16 and 17). The exothermic peaks are observed at 551 °C with heat of reaction 436.99 J g^{-1} for nano-sized materials and at 525.4 °C for micro-sized materials with ΔH of 41.52 J g^{-1}. Though the positions of the exothermic peak are the same, the nano-materials are not effective in making sound producing firecrackers whereas micro-sized particles are effective in making sound producing firecrackers. The agglomeration of nano-sized particles of $Sr(NO_3)_3$ reduces the efficiency of the firecrackers.

If $Ba(NO_3)_2$is used as oxidizer in a nano-sized mixture, one endothermic peak at 117 °C and two small exothermic peaks at 366 °C and 516 °C are observed (Figures 18 and 19). But this exothermic peak is immediately followed by an endothermic peak at 583 °C making the pyrotechnic mixture not fit for making sound producing firecrackers in this particular molar ratio. The micro-sized materials give an endothermic peak at 590 °C with no remarkable exothermic peak making the pyrotechnic mixture not fit for firecrackers.

If Bi_2O_3 is used as oxidizer (Figures 20 and 21) a sudden exothermic reaction will not take place even at high temperatures for both micro- and nano-sized materials. Bi_2O_3 can not be used as an effective oxidizer in making sound producing firecrackers.

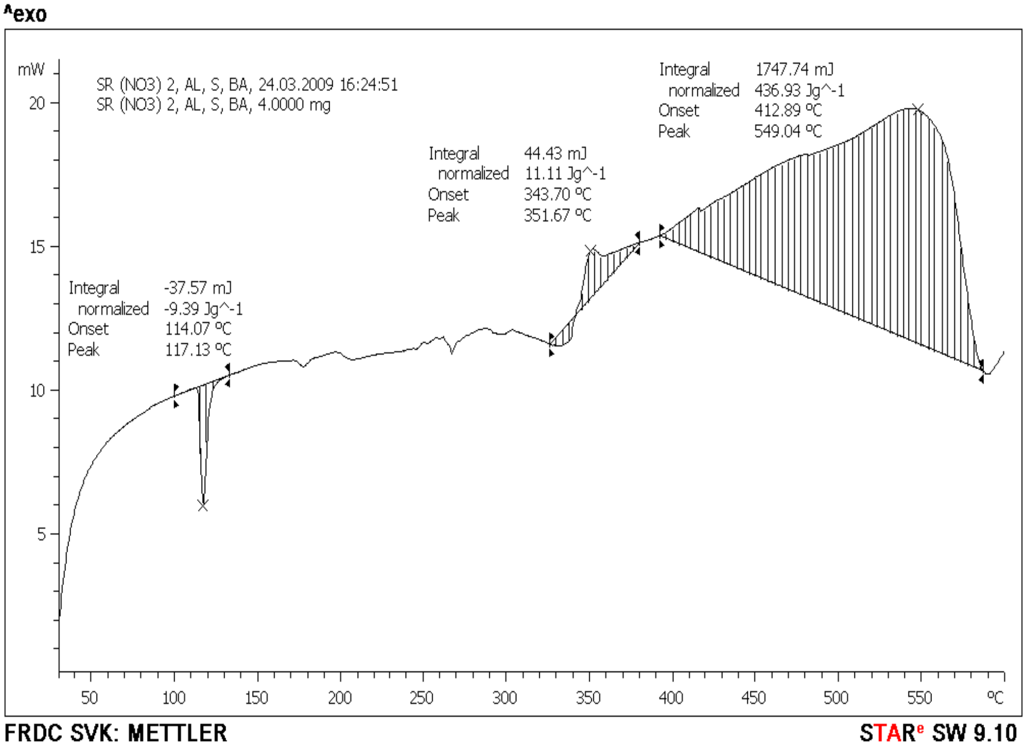

Figure 16. *DSC analysis of nano-sized pyrotechnic mixture, $Sr(NO_3)_2/S/Al/H_3BO_3$.*

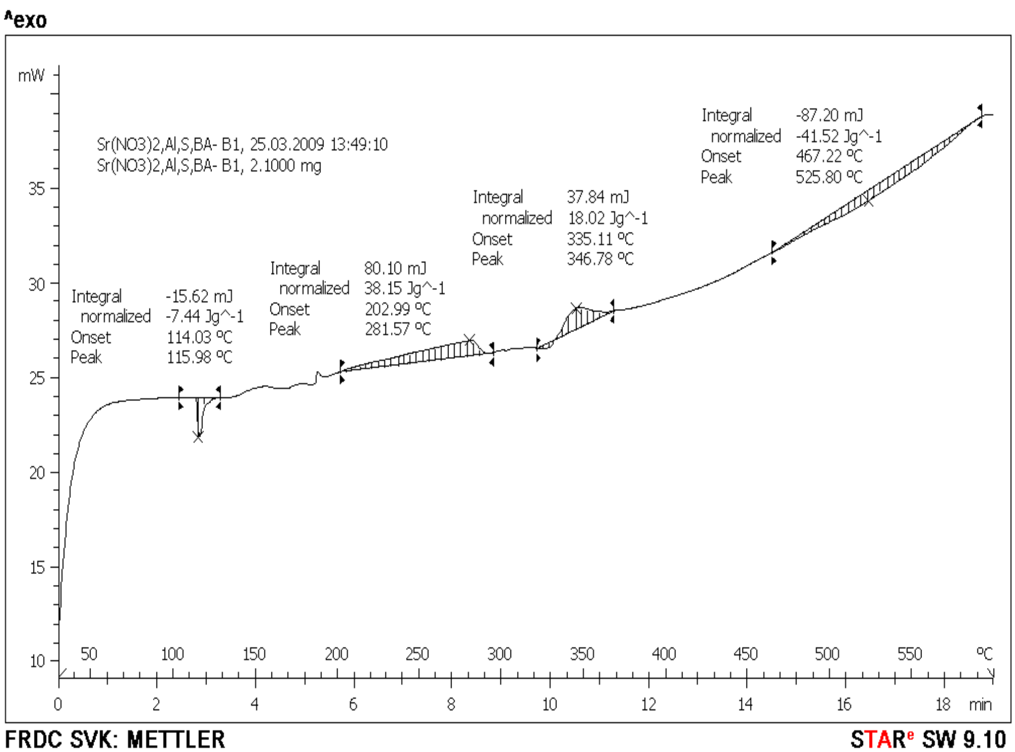

Figure 17. *DSC analysis of micro-sized pyrotechnic mixture, $Sr(NO_3)_2/S/Al/H_3BO_3$.*

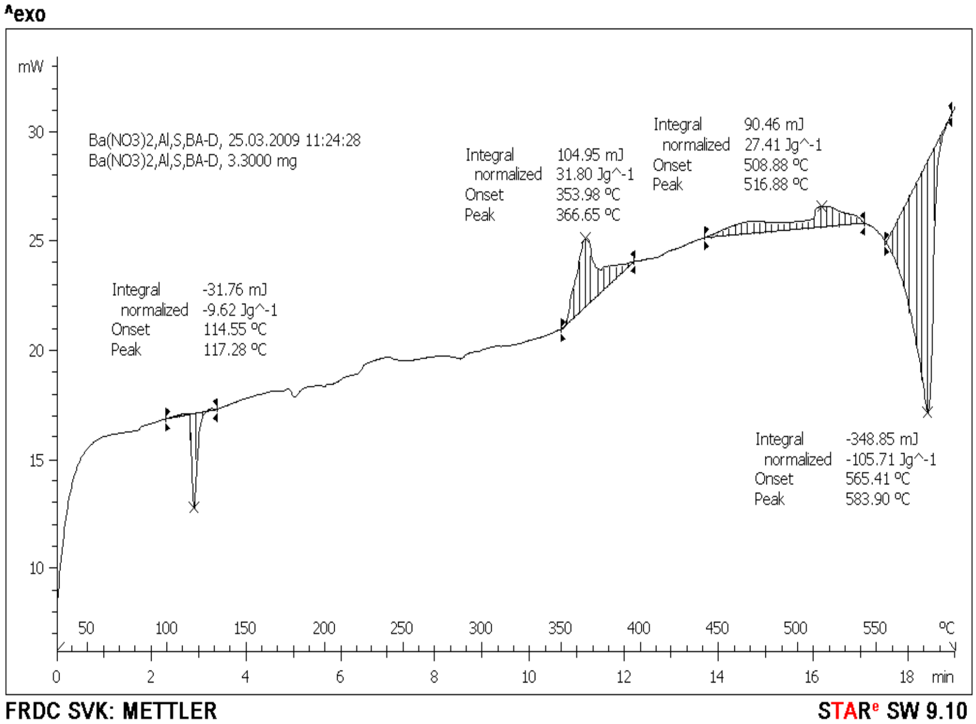

Figure 18. *DSC analysis of nano-sized pyrotechnic mixture, $Ba(NO_3)_2/S/Al/H_3BO_3$.*

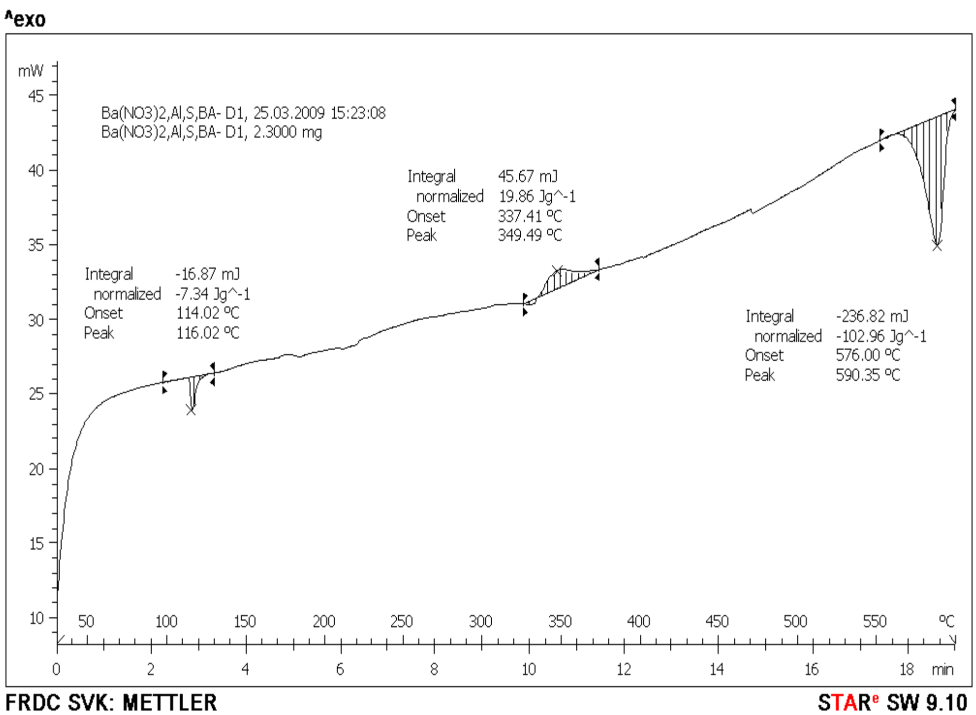

Figure 19. *DSC analysis of micro-sized pyrotechnic mixture, $Ba(NO_3)_2/S/Al/H_3BO_3$.*

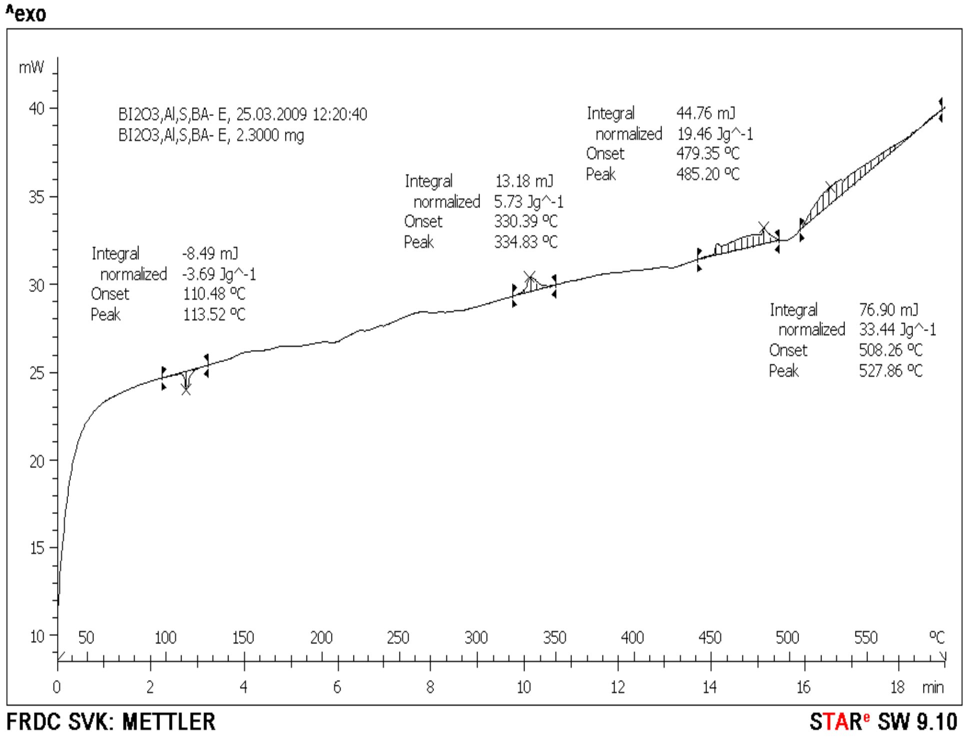

Figure 20. *DSC analysis of nano-sized pyrotechnic mixture, $Bi_2O_3/S/Al/H_3BO_3$.*

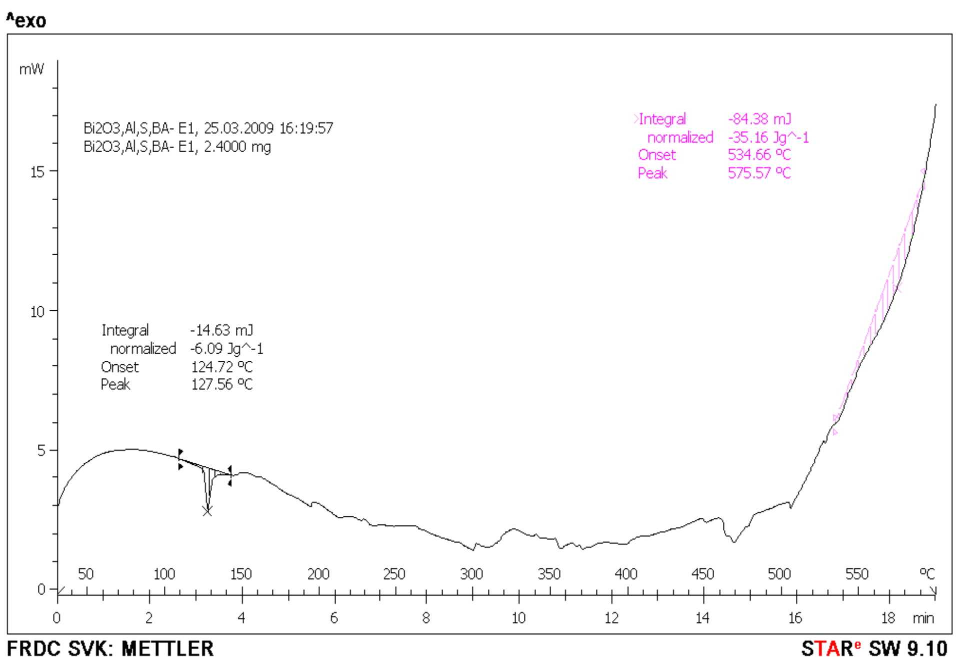

Figure 21. *DSC analysis of micro-sized pyrotechnic mixture, $Bi_2O_3/S/Al/H_3BO_3$.*

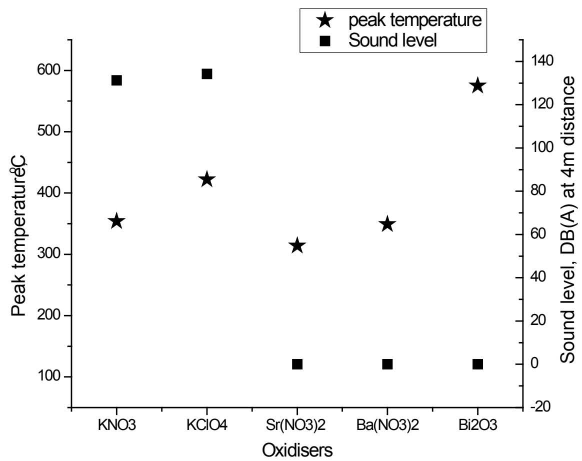

Figure 22. *Interrelation between peak temperature and sound level of nano-materials.*

Interrelation between sound level and thermal decomposition parameters

The nano-materials of the pyrotechnic mixture (Figures 22–24) reveal that there is an inverse relationship between peak temperature and ΔH, and peak temperature and sound level. A high peak temperature leads to the production of low sound level in the firecrackers. The micro-materials of pyrotechnic mixtures (Figures 24–26) reveal that there is no definite relationship between peak temperature and ΔH in the molar compositions taken for analysis. Figure 24 shows that the peak temperature of nano-materials is high compared to that of micro-materials and the difference between the peak temperature of a pyrotechnic mixture using the oxidizer strontium nitrate in nano- and micro-materials is large and the nano-materials do not produce sound which may be due to the formation of agglomeration. In a pyrotechnic mixture with the oxidizer KNO_3 or $KClO_4$, ΔH_{nano} is less than ΔH_{micro} and nano-materials were found to produce sound effectively. In the case of $Sr(NO_3)_2$, $\Delta H_{nano} > \Delta H_{micro}$ and micro-materials are effective in producing sound. It was observed that the higher the peak temperature, the lower will be ΔH.

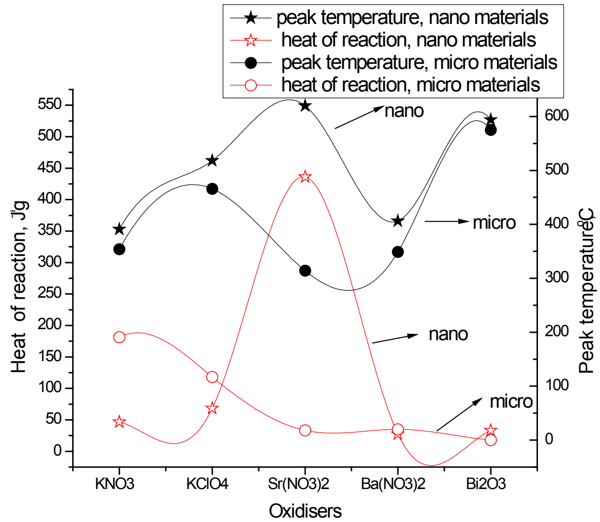

Figure 24. *Interrelation between peak temperature and heat of reaction for micro- and nano-oxidizer composition.*

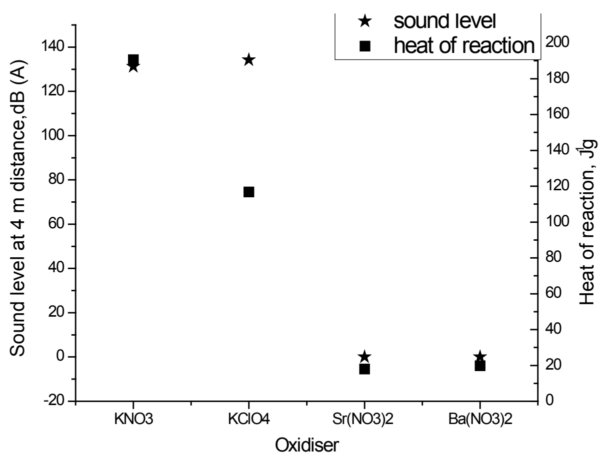

Figure 23. *Interrelation between heat of reaction and sound level of nano-materials.*

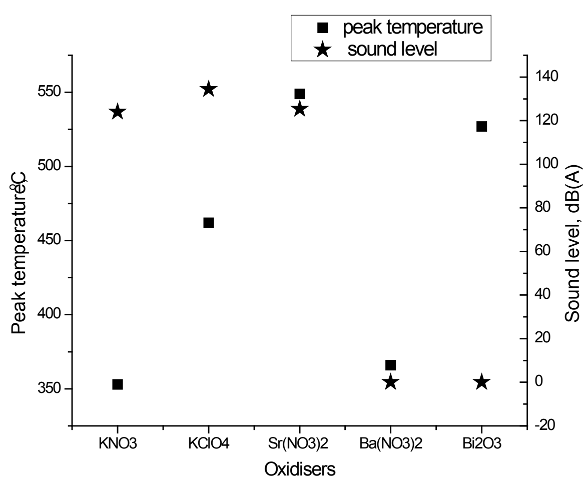

Figure 25. *Interrelation between peak temperature and sound level of micro-materials.*

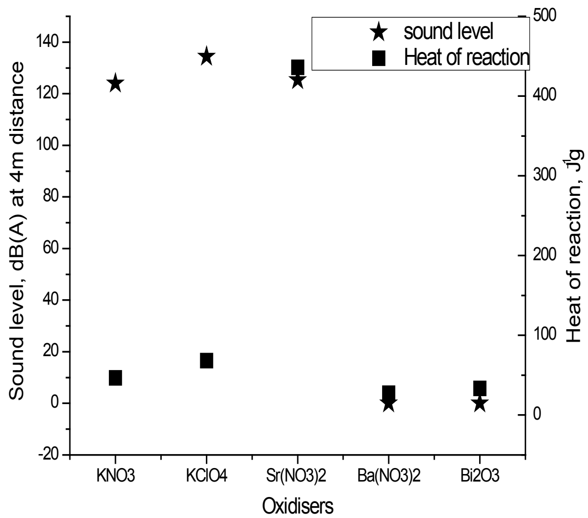

Figure 26. *Interrelation between heat of reaction and sound level of micro-materials.*

Conclusion

In sound producing cake-bomb firecrackers, pyrotechnic mixtures containing five different oxidizers with S, Al, and H_3BO_3 are used. The effect of different oxidizers in producing sound was studied and it was found that the nature of the oxidizer plays an important role. $KClO_4$ is a powerful oxidizer, thermally stable but highly sensitive to impact and friction which is not safe for keeping the pyrotechnic mixture as a loose composition and for transport. If the mixture is not used completely in the manufacturing unit, it should be destroyed in an appropriate way. Similarly, $Ba(NO_3)_2$ is also found to be an effective oxidizer but an anticaking reagent should be used for storing. The pyrotechnic mixture containing KNO_3/S/Al(H_3BO_3) whose inversion temperature is above 400 °C and which is less sensitive to mechanical stress is safe for transport. The composition consisting of 57.5% KNO_3, 20% S, 22% Al and 0.5% H_3BO_3 appears to be an ideal composition in all respects with reduced impact sensitivity, required explosivity and allowed sound pressure level.

Acknowledgements

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References

1 K. Kosanke and B. Kosanke, ‘Pyrotechnic ignition and propagation: A review’, in *Pyrotechnic Chemistry*, Vol. 4, Journal of Pyrotechnics, USA, 2004, Chapter 4, pp. 1–10.

2 B. Thomson and A. Wild, ‘Factors affecting the rate of burning of a titanium–strontium nitrate based compositions’, *Proceedings of Pyrochemical International*, United Kingdom, 1975.

3 S. Sivaprakasam and M. Surianarayanan, ‘Interrelation between impact, friction, and thermal energy in a pyrotechnic flash reaction’, *Journal of Pyrotechnics,* Vol. 23, 2006, p. 51.

4 *Gazette Notification*, 1999, Noise Standards for Firecrackers, *G. S. R 682(E)*.

5 A. JeyaRajendran and T. L. Thanulingam, ‘Sound level analysis of firecrackers’ *Journal of Pyrotechnics,* Vol. 27, 2008, pp. 60–76.

6 H. Koenen, K. Ide and K. Swart, *Pruefverfahren der Bundesanstalt fuer Materialforschung und -pruefung (BAM)* Vol. 94, 1961, p. 30.

7 R. Wharton and J. Harding, ‘An experimental comparison of three documented methods for the evaluation of friction sensitiveness’, *Journal of Energetic Materials,* Vol. 11, 1993, pp. 51–65.

8 R. K. Wharton, R. J. Rapley and J. A. Harding, ‘The mechanical sensitiveness of titanium/blackpowder pyrotechnic compositions’, *Propellants, Explosives, Pyrotechnics,* Vol. 18, 1993, pp. 25–28.

9 *United Nations: Recommendations on the Transport Dangerous Goods, Manual of tests and criteria*, United Nations, New York, 1990; Vol. ST/SG/AC.10.11/Rev 3.

10 M. Fathollahi, S. Pourmortazavi and S. Hosseini, ‘The effect of particle size of $KClO_3$ in pyrotechnic compositions’, *Combustion and Flame*, Vol. 138, 2004, pp. 304–306.