

Sound Level Analysis of Firecrackers

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Abstract: The noise levels from sound-producing firecrackers, both commercial and newly formulated, were measured. Commercial sound-producing firecrackers produce noise in the range of 130.7 dB(A)/150.4 dB(C) peak to 142.8 dB(A)/162.6 dB(C) peak at a distance of 4 m. A set of pyrotechnic compositions of potassium nitrate (KNO_3), sulphur (S), aluminium (Al) and boric acid (H_3BO_3) was used to produce different varieties of sound-producing firecrackers for analysis. A bulk density of $0.44\text{--}0.50\text{ g cm}^{-3}$ was maintained for homogeneity of the mixture. The factors influencing the sound from firecrackers, such as amount of mixture, weight percentage of oxidizer and fuel, particle size of the ingredients, bursting strength of the paper used for the inner paper case of the firecracker unit and variation in percentage composition, were studied. The noise level produced from different sizes of firecracker units shows a linear relationship with the weight of the mixture used and the bursting strength of the paper. It was found that the pyrotechnic mixture of composition 57.5/20/22/0.5% $\text{KNO}_3/\text{S}/\text{Al}/\text{H}_3\text{BO}_3$ in a firecracker unit made from 240 gsm kraft paper and bursting strength 2.2 kg cm^{-2} produced allowed sound levels of $<125\text{ dB(A)}/145\text{ dB(C)}$ peak at 4 m distance. The efficiency of the pyrotechnic mixture for making fireworks is explained by measuring the safety characteristic data of thermal and mechanical sensitivity. Furthermore, a comparison between a mixture containing potassium chlorate, i.e. $\text{KClO}_4/\text{S}/\text{Al}/\text{H}_3\text{BO}_3$, and $\text{KNO}_3/\text{S}/\text{Al}/\text{H}_3\text{BO}_3$ was made on the basis of sensitivity measurements. The limiting impact energy (LIE) of pyrotechnic flash compositions of $\text{KNO}_3/\text{S}/\text{Al}/\text{H}_3\text{BO}_3$ falls in the range of 5.3 J making the mixtures class III explosives. The ignition temperature was found using differential scanning calorimetric (DSC) analysis to be in the region of $437.9\text{--}498\text{ }^\circ\text{C}$. Self-propagating decomposition occurred only at high temperatures for $\text{KNO}_3/\text{S}/\text{Al}/\text{H}_3\text{BO}_3$ making the mixture thermally stable.

Keywords: Sound level, noise level, pyrotechnic mixture, impact sensitivity, friction sensitivity, flash composition, firecrackers.

Introduction

Fireworks are made from pyrotechnic mixtures of an oxidizer and a fuel and, optionally, a colour enhancing chemical and a binder. The chemicals employed and their compositions vary depending on the type of firework being produced. Fireworks are of two types, light-producing and sound-producing. Magnesium powder is frequently employed as a fuel for high light output and magnesium fuel is replaced by another metallic fuel in combination with sulphur

for high sound output.¹ Pyrotechnic mixtures are energetic compounds susceptible to explosive degradation on ignition, impact and friction and are obtained by mixing finely divided (reducing) metal powders with inorganic oxidizing agents that are capable of undergoing self-sustaining combustion.² The compositions have a wide range of applications utilizing the production of light, heat, sound or smoke.³ Pyrotechnic compositions used for firecrackers differ from explosives and propellants in that they do not necessarily give rise to a violent expansion of gas

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and their rate of reaction is normally considerably less than that of either explosives or of recognized propellants. During the firework manufacturing process, 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 results from burning a particular pyrotechnic composition depend on various factors. Chemicals used as additives even in small quantities to improve the mechanical properties can alter the combustion process and lower the ignition temperature. The effectiveness of firecrackers depends not only on the composition of the mixture, but also on factors such as particle size and shape, choice of fuel and oxidizer, 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.⁴

As per the Indian Explosives Act, 1884, using a mixture of chlorate and sulphur is prohibited due to its ease of ignition and sensitiveness to undergo explosive decomposition.⁵ Alternative mixtures have been widely used in the fireworks industry and accidents still occur. The main reason is poor understanding of the explosive nature and lack of mechanical and thermal sensitivity data for mixtures used in the firework industry. In the past, researchers have studied the thermal and mechanical sensitivity of sulphur and chlorate mixtures.^{6,7} Very little work on the impact sensitivity of mixtures containing $\text{KNO}_3/\text{S}/\text{Al}$ has been reported.^{8,9} However, the analysis of sound levels produced from firecrackers and ways to control sound levels have not yet been reported. As per the Government of India notification 'Sound emitting fire crackers with sound level exceeding 125 dB(A) or 145 dB(C) peak at 4 m distance from the point of bursting are prohibited.'¹⁰ The present work focuses on analysing the noise levels produced from commercially available firecrackers at 4 m distance and on controlling the sound levels within the allowed limits by varying parameters such as amount of mixture used, weight percentage of oxidizer and fuel, particle size of the ingredients, bursting strength of paper used for making the shell, and composition. The study also assesses

the impact and friction sensitivity of the optimized pyrotechnic mixture for safety considerations and to classify the pyrotechnic mixture according to the Andreiev-Beliaev classification.¹¹ The study helps to choose an ideal composition so that environmental pollution due to excessive usage of chemicals and noise pollution can be minimized.

Experimental

Chemicals and materials

The chemicals used for the preparations of the firecrackers were obtained from a firework manufacturing company situated in the southern state of Tamilnadu, India. The purity and assay of the chemicals were KNO_3 97.6%, S 99.9%, Al 99.8% and H_3BO_3 99%. Aluminium powders of grade 999 (200 mesh, 75 micron), potassium nitrate of 120 mesh (125 micron), sulphur of 100 mesh (150 micron) and boric acid of 100 mesh (150 micron) sizes were used for making fireworks. All these chemicals were sieved through a 100 mesh brass sieve. The samples were stored away from light and moisture until they were packed inside the paper case of the fire cracker unit (Figure 1). Two types of papers, kraft paper (brown) and duplex board (white) with different thicknesses which were measured by a GSM meter (gram per square metre) were used for making the inner shells of the firecrackers. Jute string with gum of length 130–260 cm and thin foil paper (cello paper) were used for making the firecrackers. Three types of paper cases, small ($15 \times 15 \times 15$ mm; 3.375 cm^3), large ($28 \times 15 \times 15$ mm; 6.3 cm^3) and $28 \times 28 \times 15$ mm (11.76 cm^3) (Figure 1) were used to prepare cake-bomb, hydrogen-bomb and thunder-bomb firecrackers respectively similar to commercially available firecrackers.

Firecrackers

Three types of firecrackers like the cake-bomb, hydrogen-bomb and thunder-bomb were manufactured manually by experienced technicians from a firework manufacturing company situated in the southern state of Tamilnadu, India, for analysis. The chemical mixture of potassium nitrate, sulphur, aluminium, and boric acid in the ratio 57.5 : 20 : 22 : 0.5% and the chemicals were sieved separately and mixed thoroughly on non-conducting surfaces like newspaper, rubber mat etc., by sieving through a No. 40 mesh (425 micron),



Inner paper case (large)



Fire cracker (hydrogen bomb)

Figure 1. Firecracker used for analysis.

4 to 5 times to get a homogeneous mixture. This chemical mixture was used to fill 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; 3 windings were done and it was dried in sunlight for 2 to 3 hours. The fuse wire (100 mm, quick match) was inserted with the help of a brass needle and kept in place with charcoal powder. Coloured fancy papers were used to cover the case for appearance and it was dried for about 24 hours in sunlight to make the firecrackers ready for testing. The compositions used to make firecrackers for analysis are given in Table 1.

Instruments

Sound level tester

Sound level tests were carried out as per the rules of notification of PESO (Petroleum and Explosives Safety Organisation), formerly known as ‘Dept. of Explosives’, Govt. of India.⁹ The noise level was measured with 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. 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. While 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 sound level measurements were made with four approved sound level meters simultaneously, equally spaced apart 90° at 4 m distance from the bursting place in a circle, at a height of 1.2 m (Figure 2). A 5 m diameter hard concrete surface was considered as free-field

Table 1 composition of chemicals used in firecrackers.

Component	% Range
KNO ₃	65–50
S	24–5
Al	44.5–14.5

Table 2 Impact sensitivity of standards to calibrate the impact sensitivity 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

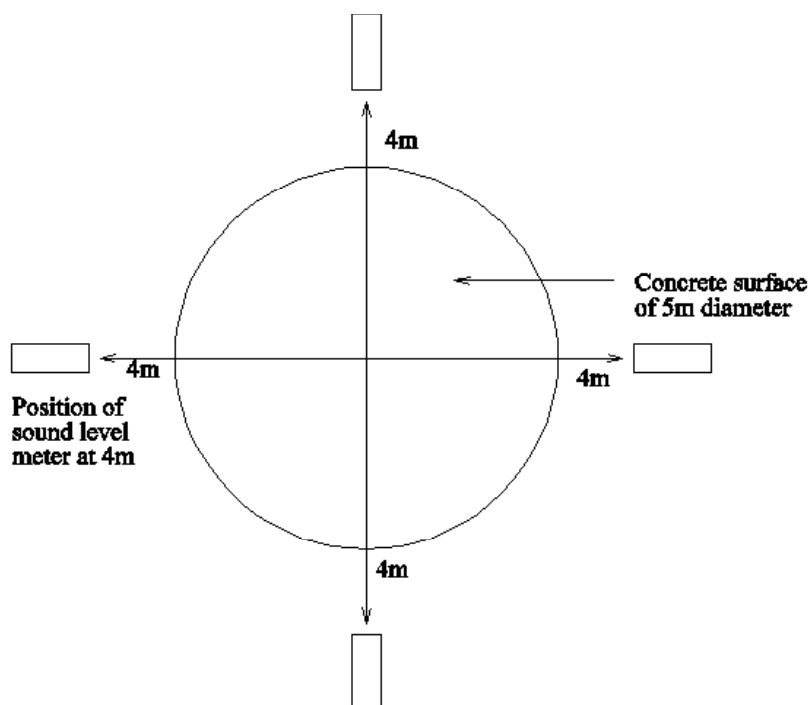


Figure 2. Sound level analysis on site-free field conditions.

Table 3 Sound level analysis of commercial firecrackers

Sr. No	Source	Trade name of firecrackers	Outer dimensions (mm)	Sound level/ db(A)	Sound level/ dB(C) peak
1	Fireworks Factory I, Sivakasi	Cake-bomb	30 × 20 × 20	137.6	149.2
		Hydrogen-bomb	38 × 20 × 20	134.9	151.6
2	Fireworks Factory II, Sivakasi	Hydrogen-bomb	35 × 20 × 20	136.0	153.3
		Atom-bomb	35 × 20 × 20	134.9	151.6
		Classic-bomb	40 × 35 × 20	134.9	151.6
3	Fireworks Factory III, Sivakasi	Atom-bomb green	40 × 20 × 20	136.0	153.3
		Atom-bomb	25 × 30 × 20	133.9	151.5
		Hydrogen King green bomb	40 × 30 × 20	140	152.2
4	Fireworks Factory IV, Sivakasi	Atom-bomb small	25 × 20 × 20	130.7	150.4
		Atom-bomb big	32 × 25 × 20	133.1	153.4
		Hydrogen-bomb	40 × 28 × 20	135.3	155.0
		Kingkong bomb	35 × 35 × 20	136.1	157.3
5	Fireworks Factory V, Sivakasi	Rectangular bomb	20 × 20 × 20	129.9	149.4
		Minibullet	25 × 19 × 20	126.4	146.2
		Neutron-bomb	31 × 18 × 20	132.8	153.8

Table 4. *Effect of amount of pyrotechnic mixture on sound level.*

Types of atom-bomb	Wt of chemicals/g	Sound level/dB(A)	Sound level/dB(C) peak
Cake-bomb ^a	0.5	107.6	131.0
	0.75	113.2	136.3
	1.00	123.8	144.1
	1.25	128.1	151.8
	1.50	133.8	156.2
Hydrogen-bomb ^b	0.75	109.6	135.1
	1.00	113.5	137.8
	1.25	119.8	143.1
	1.50	124.0	144.1
	1.75	128.1	149.8
	2.00	133.5	155.9
Thunder-bomb ^c	1.00	109.6	135.1
	1.50	113.5	137.8
	2.00	122.3	143.1
	2.50	132.4	155.0
	3.00	135.4	158.3
	3.50	135.5	158.6
	4.00	138.6	160.8

^a Inner box dimension: $15 \times 15 \times 15 \text{ mm}^3$ (3.375 cm^3); jute length 130 cm, winding: 3 ply, GSM 240 g m^{-2} , bursting strength 2.2 kg cm^{-2} . ^b Inner box dimension: $28 \times 15 \times 15 \text{ mm}^3$ (6.3 cm^3); jute length: 195 cm, winding: 3 ply, GSM 240 g m^{-2} , bursting strength 2.2 kg cm^{-2} . ^c Inner box dimension: $28 \times 15 \times 28 \text{ mm}^3$ (11.76 cm^3); jute length: 260 cm, winding: 3 ply, GSM 240 g m^{-2} , bursting strength 2.2 kg cm^{-2} .

conditions for carrying out the sound level test. A microphone converted sound into electrical power and a decibel meter read out the sound power in watts or dB.

Impact sensitivity tester

Impact sensitivity of the pyrotechnic mixture was tested using the BAM method^{12,13} with an Impact sensitivity tester, supplied by Electro Ceramic Private Limited, Pune, India. The design and principles of the equipment are similar to those of the BAM standard drop fall hammer equipment. The procedure followed in this study was based on a previously reported method.⁹ LIE of the sample was calculated using the formula,

$$\text{LIE} = mgh$$

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 2. The impact energy measured was within acceptable limits of error (1–2%). Several runs were undertaken to check the reproducibility.

Friction sensitivity tester

The friction sensitivity was determined using a Friction Tester by the general test methods of BAM¹² and corresponds to the UN Recommendations on the Transport of Dangerous Goods.¹³ The friction test determines whether a pyrotechnic mixture possesses a danger of explosion or reaction when subjected to the effects of friction. When starting a test, a weight of materials was chosen

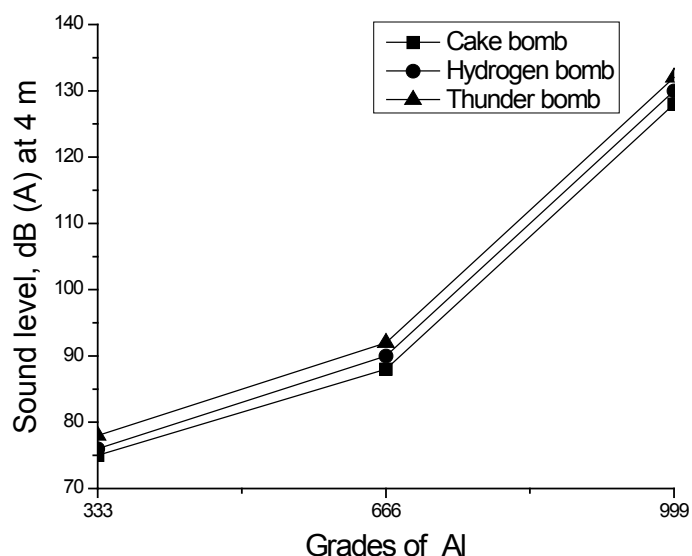


Figure 3. *Effect of particle size.*

approximately in the middle of the loading range. If two reactions were detected, then the load would be decreased. If no reaction occurred, then the load would be increased. Friction sensitivity is a relative measurement reported in newtons (N), when inflammation or explosion occurs only once in six repetitions.

Thermal analyser

Thermal analysis (TA), thermogravimetric (TG) and differential thermal analysis (DTA) was carried out using a Perkin-Elmer Pyris diamond model thermal analyser with a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$, $30\text{ }^{\circ}\text{C min}^{-1}$ and $50\text{ }^{\circ}\text{C min}^{-1}$ and a temperature range of the standard system from room temperature to $1100\text{ }^{\circ}\text{C}$.

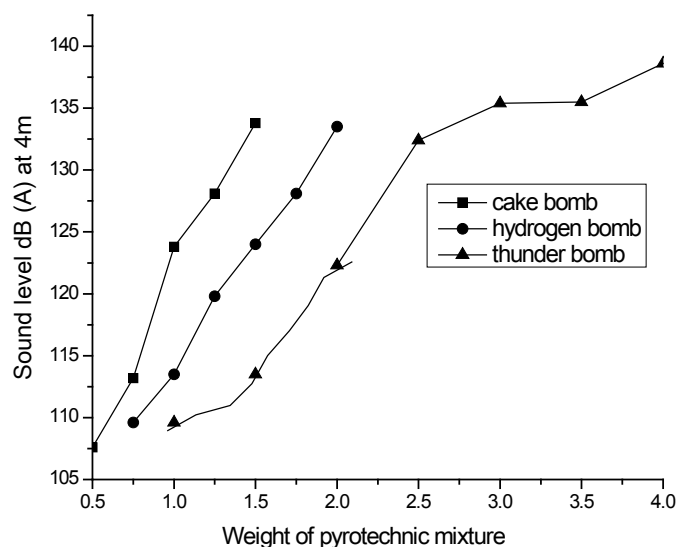


Figure 4. *Effect of the amount of pyrotechnic mixture on sound level.*

Table 5. *Effect of the quality of paper of the inner shell on sound level.*

Dimension of the shell	Weight of pyrotechnic mixture/g	Paper weight (GSM)/g m ⁻²	Bursting strength/kg cm ⁻²	Sound level/ dB(A)	Sound level/ dB(C) peak
Cake-bomb	1.0	120 ^a	2.4	128.5	143.1
		180 ^a	3.2	129.4	148.0
		240 ^a	2.2	123.6	142.1
Hydrogen-bomb	1.5	120 ^a	2.4	125.0	146.5
		180 ^a	3.2	132.8	155.5
		240 ^a	2.2	124.0	144.1
Thunder-bomb	2.0	120 ^a	2.4	127.0	148.5
		180 ^a	3.2	128.6	149.7
		240 ^a	2.2	122.3	145.3
		270 ^b	4.1	129.4	150.2
		320 ^b	5.4	131.2	153.0

^aKraft paper (brown). ^bDuplex board (white)

Differential scanning calorimetry

A Differential Scanning Calorimetry (DSC) module 821 from Mettler Toledo TA instruments was used for thermal stability measurements under ignition conditions. The studies were conducted by using 2 mg sample in an aluminium sample holder under pure nitrogen gas as purge gas and

an air flow rate of 50 ml min⁻¹ with a temperature range of -65 °C to 450 °C and a heating rate of 10 °C min⁻¹ and the air flow rate was maintained as 50 ml min⁻¹.

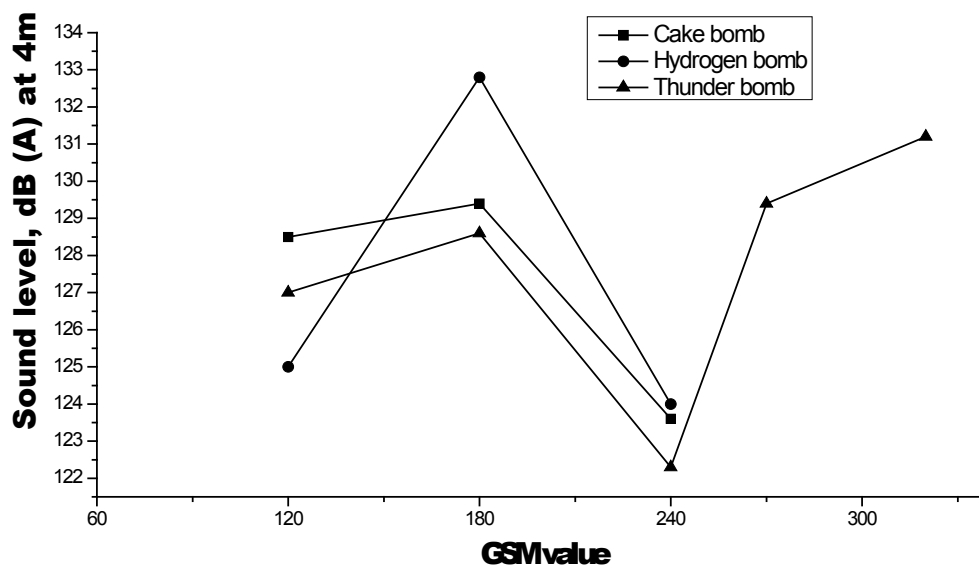
**Figure 5.** *Effect of GSM value on the bursting strength of paper.*

Table 6 Sound level analysis of firecrackers made by different chemical composition

Sample No.	Compositions (wt%)			Onset temp./°C	Peak temp./°C	$\Delta H/J\ g^{-1}$	Sound level	
	KNO ₃	S	Al				dB(A)	db(C) peak
1	50	5	44.5	461.2	491.08	48.45	105.8	125.4
2	50	9.5	40.0	442.04	493.67	106.89	119.8	139.5
3	50	20	29.5	432.14	492.51	120.14	134.8	154.4
4	50	22	27.5	431.56	491.68	118.56	127.2	147.1
5	52.5	20	27.0	434.17	494.16	126.56	132.8	152.6
6	55	20	24.5	435.48	496.34	132.78	130.7	150.4
7	56	20	23.5	436.86	496.88	139.67	129.4	149.0
8	57.5	20	22.0	437.99	498.77	144.62	125.0	144.6
9	57.5	8	34.0	452.17	492.84	96.12	116.0	136.3
10	57.5	16	26.0	434.65	496.71	146.78	128.1	148.4
11	57.5	24	18.0	442.43	492.83	142.67	121.8	141.6
12	58	20	21.5	437.11	497.74	141.52	126.6	148.3
13	60	20	19.5	436.23	498.01	146.87	127.4	147.2
14	62.5	20	17.0	435.82	495.74	138.85	128.8	148.3
15	65	20	14.5	435.67	493.48	134.89	130.3	150.1

1.5 g of firecracker mixture with 0.5% H₃BO₃ in a paper case of inner box dimension of 28 × 15 × 15 mm³ (6.3 cm³); paper case: GSM 240 g m⁻² and bursting strength 2.2 kg cm⁻². Jute length: 195 cm, winding: 3 ply.

Paper quality analysis

The bursting strength of the paper used for making the inner case of the firecrackers was measured using a bursting strength tester (Analog model) and the thickness of the paper was measured using a GSM meter (Analog model).

Results and discussion

Sound level analysis of commercial firecrackers

Commercial sound producing firecrackers were obtained from five different well known companies situated in Sivakasi, India. Sound level analysis was carried out and the data are given in Table 3. Commercial sound producing firecrackers produce sound levels in the range 130.7 dB(A₁)/150.4 dB(C) peak to 142.8 dB(A₁)/162.6 dB(C) peak at 4 m distance which is much higher than the allowed sound level of 125 dB/140 dB(C) peak. The sound level was measured on varying the following factors.

Effect of particle size

The effect of sound level from different types of firecracker with different grades of Al based on the particle size was studied (Figure 3). It is clear that as the particle size decreases, the pyrotechnic mixture is effective in producing sound.¹⁴ Al of grades 333 (60 mesh/250 micron size) and 666 (100 mesh/150 micron size) could produce flash instead of producing sound while Al of 999 grade (200 mesh/63 micron size) alone produces sound effectively. Sound level tests were conducted on varying the particle size of KNO₃ in the range 63–250 micron. It was found that increasing the particle size of KNO₃ decreased the sound level but the effect is much smaller than that of the variation of aluminium particle size. This trend was due to the fact that the sound produced depends not only on the composition and the particle size but also on the particle shape, density and compactness of the chemicals. In order to maintain homogeneity of the mixture, the bulk packing density was maintained at 0.44–0.50 g cm⁻³.

Table 7. Correlation of sound level and thermal decomposition temperature.

Variables	Correlation coefficient	Significance
Sound level vs. onset temperature	−0.9445	A strong negative correlation
Sound level vs. peak temperature	−0.9025	A strong negative correlation
Sound level vs. heat of reaction	−0.9555	A strong negative correlation

Effect of size and quality of paper case

Sound levels produced from firecrackers with inner paper cases (paper box) of different dimensions are given (Table 4). Three different sizes of case were used and the amount of the firecracker mixture required to produce the sound level increases with increasing dimensions of the box (Figure 4). The amount of firecracker mixture required to produce the allowed sound level was optimised as 1.0/1.5/2.0 g for small firecrackers (cake-bomb) and large firecrackers (hydrogen-bomb and thunder-bomb) respectively. If excess mixture is kept in the paper case of the firecrackers, the sound level produced would be higher than the allowed level.

The sound level produced from firecrackers made with different thicknesses of paper for the inner paper case was measured (Table 5). As the GSM value increases, the quality of the paper changes from paper to board. No linear relationship exists between the GSM value and the bursting strength of the paper in the case of kraft paper (brown) while the bursting strength of the paper increases with GSM value of the duplex board paper (Figure 5). kraft paper with a GSM value of 240 and bursting

strength of 2.2 kg cm^{-2} was found to produce the optimum sound level. The noise level produced from the firecrackers increases as the bursting strength of the paper increases (Figure 6).

It is possible to produce commercially available firecrackers, using 999 grade aluminium (63 micron size), an optimum quantity of pyrotechnic mixture in an inner box of specified dimensions made up with kraft paper of GSM 240, bursting strength 2.2 kg cm^{-2} , which can produce a sound level of <125 dB(A)/145 dB(C) peak at 4 m distance, within the allowed limits as prescribed by the Govt. of India notification.¹⁰

Effect of composition on sound level

The composition of the pyrotechnic mixture plays an important role. If the total content of KNO_3/S is high or without using metallic fuel, Al, then the pyrotechnic mixture is not useful for making sound-producing firecrackers; instead it produces dark fumes.¹⁵ Good thermal conductivity is essential for smooth propagation of burning. Metals are the best thermal conductors for the transfer of heat for the KNO_3/S mixture. The results of sound level tests for the different compositions are given in Table 6. It was observed that the sound level varied when the concentration of any one of the components was changed. The plot between the heat of reaction and sulphur concentration (Figure 7) showed that with increasing sulphur concentration, the decomposition energy release increased. It reached a maximum value at 16 wt% of sulphur when the concentration of KNO_3 is 50 wt% and at 20 wt% of sulphur when the concentration of KNO_3 is 57.5 wt% and then started decreasing. The concentration of sulphur appeared critical. In Table 6, it is clear that the optimum level of sound is produced in the mixture of composition $\text{KNO}_3/\text{S}/\text{Al}/\text{H}_3\text{BO}_3$ 57.5/20/22/0.5%.

Table 8 Sensitivity measurements of pyrotechnic mixtures.

Pyrotechnic composition Mass fractions (%)	Ignition temperature/°C	Friction sensitivity/N	Impact sensitivity/J
$\text{KNO}_3/\text{Al}/\text{S}/\text{H}_3\text{BO}_3$ 57.5/20/22/0.5	440	324	5.3
$\text{KClO}_4/\text{Al}/\text{S}/\text{H}_3\text{BO}_3$ 57.5/20/22/0.5		168	1.96

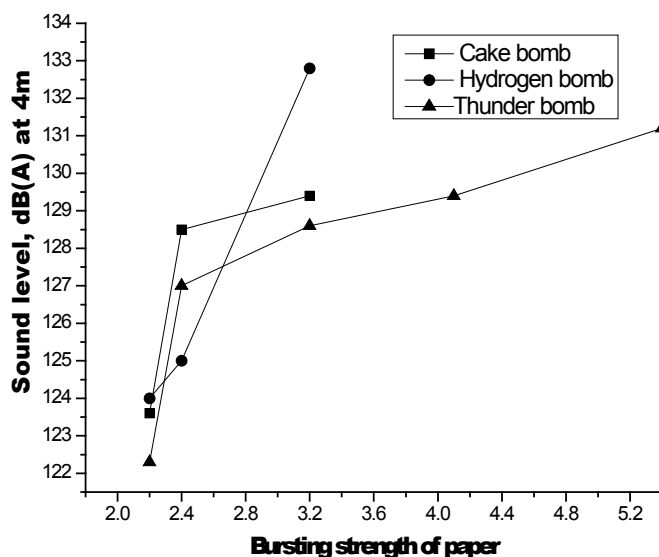


Figure 6. Effect of bursting strength of paper on sound level.

Interrelation between sound level and thermal decomposition parameters

The thermal decomposition data were subjected to Karl Pearson's correlation analysis to understand the interrelation between sound level and thermal decomposition parameters and the results are given in Table 7 and in Figures 8 and 9. Correlation analysis refers to the techniques used in measuring

the closeness of the relationship between the variables. If two variables vary such that change in one variable affects the change in the other variable, the variables are correlated. The degree of correlation is measured by correlation analysis and expressed in terms of correlation coefficient or correlation index. Karl Pearson's coefficient of correlation (r) is simple and highly reliable and r

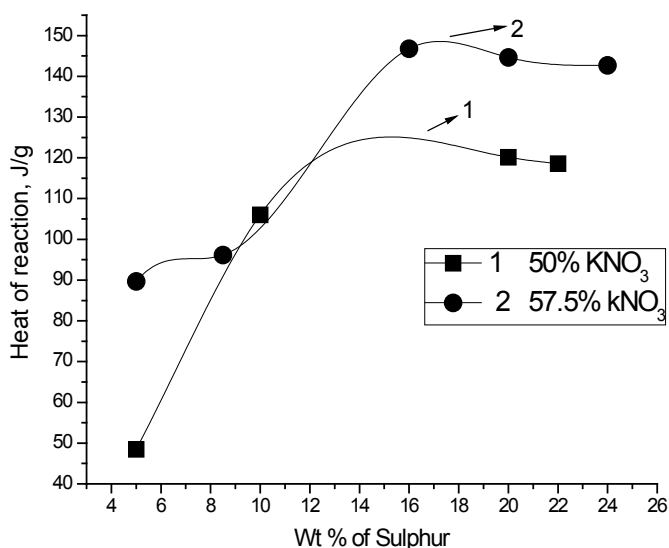


Figure 7. Effect of concentration of sulphur on the heat of decomposition.

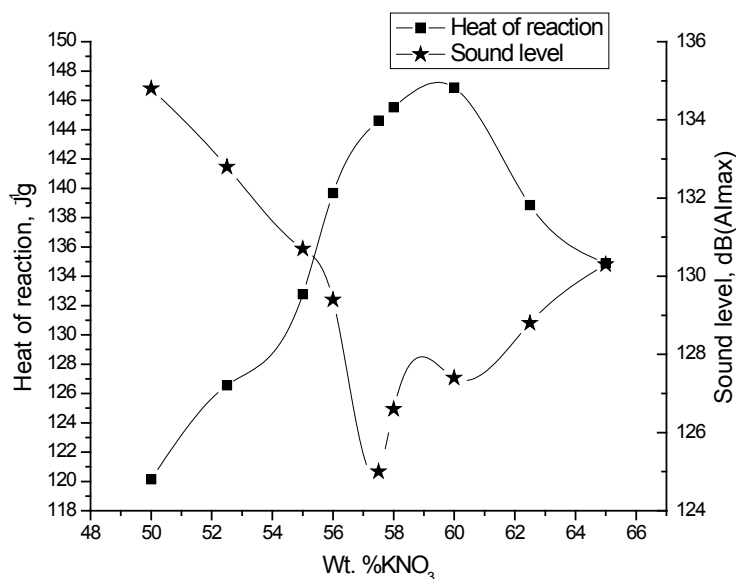


Figure 8. Interrelation between heat of reaction and sound level at fixed $S = 20$ wt%.

between any two variables, X and Y , is given as follows (equation 1):

$$r = \frac{n \sum XY - \sum X \sum Y}{\left[n \sum X^2 - \left(\sum X \right)^2 \right] \left[n \sum Y^2 - \left(\sum Y \right)^2 \right]}$$

where n = number of observations and Σ = summation.

The value of the correlation coefficient r always lies between +1 and -1. If the value of $r = 0$, then the variables X and Y indicate no correlation. If the value of r is near +1, then the variables X and Y are said to be positively correlated and if the value of r is near -1, then the variables X and Y are said to be negatively correlated.

Interrelation between the weight % of oxidiser and sound level

The results of the experiments conducted using DSC for the different compositions of firecrackers are given in Table 6. The heat of reaction, ΔH , increases with increasing concentration of KNO_3 to a maximum between 56 and 60% and ΔH decreases above 62 wt% of KNO_3 . The region 56–60 wt% of KNO_3 is considered as critical to the sound level produced. A strong negative correlation

coefficient $r = -0.9555$ (Table 7) reveals an inverse relationship between noise levels and ΔH which was determined by DSC analysis (Figure 8).

Interrelation between peak temperature and sound level

The interrelation between peak temperature (Table 6) which was determined by DSC analysis and sound level at a fixed sulphur concentration ($S = 20$ wt%) is given graphically in Figure 9. High peak temperature leads to the production of low sound levels in the firecrackers in the region of 56 and 60% KNO_3 , very similar to the plot of ΔH vs. sound level (Figure 8). A strong negative correlation coefficient, $r = -0.9025$ (Table 7) reveals the inverse relationship between sound level and peak temperature.

Mechanical sensitivity measurements

Friction sensitivity

A study of the sensitivity of the pyrotechnic mixture $\text{KNO}_3/\text{S}/\text{Al}/\text{H}_3\text{BO}_3$ 57.5/20/22/0.5% was carried out (Table 8) to indicate the explosivity nature of the pyrotechnic mixture. The sensitivity to mechanical stress like friction and impact sensitivity of the pyrotechnic mixture was measured.¹⁶ The friction sensitivity is found to be 324 N. High measurements indicate low friction

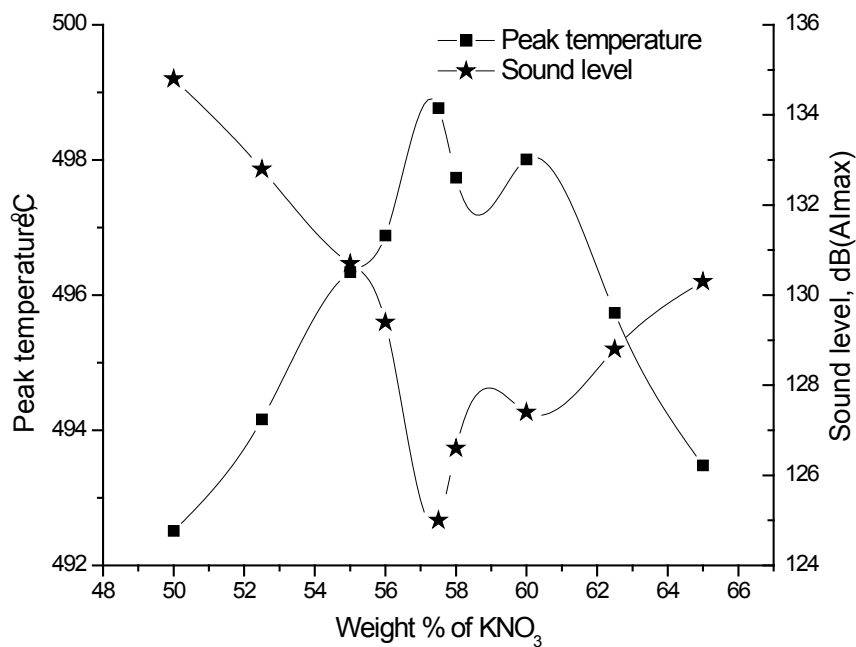


Figure 9. Interrelation between peak temperature and sound level at fixed $S = 20$ wt%.

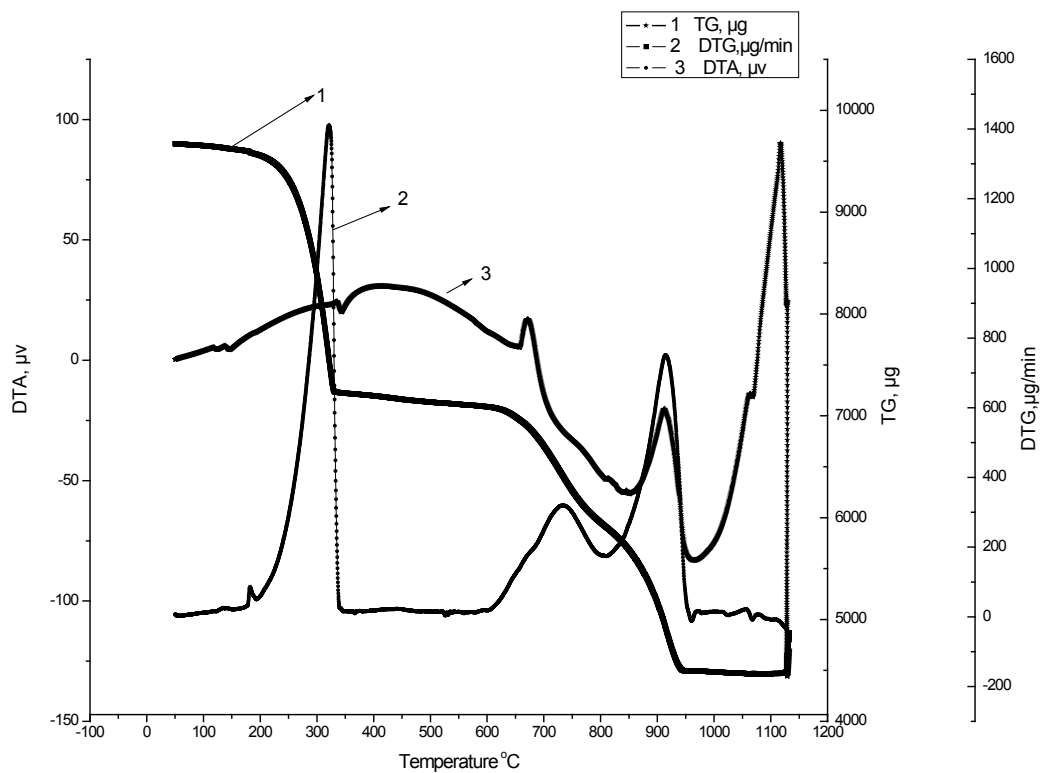


Figure 10. Thermogram of pyrotechnic mixture (at a heating rate of $30\text{ }^{\circ}\text{C min}^{-1}$).

sensitivity and the pyrotechnic mixture is safe from accidental risk of mechanical stress.¹⁷ Any material with a limiting load less than 80 N is considered too sensitive for transport of military pyrotechnics. In the case of firecrackers, any material that produces a ‘Threshold of Initiation’ (TIL) greater than 184 N is deemed to be fit for transport.¹⁷ In order to compare the sensitivity of pyrotechnic mixtures, a highly sensitive pyrotechnic mixture of $\text{KClO}_4/\text{S}/\text{Al}(\text{H}_3\text{BO}_3)$ in the same proportions was tested for sensitivity and it was found to be 168 N which is <184 N making it too sensitive for transport.

Impact sensitivity

The impact sensitiveness of the pyrotechnic mixture was measured in terms of the LIE (Table 8). The limiting impact energy was 5.3 J for the firecracker compositions $\text{KNO}_3/\text{S}/\text{Al}/\text{H}_3\text{BO}_3$ (LIE for $\text{KClO}_4/\text{S}/\text{Al}/\text{H}_3\text{BO}_3$ is 1.9), so they could

be treated as category III explosives according to the classification of Andreiev-Beliaev¹¹ indicating that this composition was sensitive to impact. This impact sensitivity indicated that the mixture was prone to hazards from impact and at the same time it could be used to produce good firecrackers.

Thermal analysis

In order to understand the sensitivity of the material to heat and to determine the relative onset decomposition temperature, thermal analysis of the composition $\text{KNO}_3/\text{S}/\text{Al}/\text{H}_3\text{BO}_3$ as 57.5/20/22/0.5% was carried out (Figure 10) at the three different heating rates of 10, 30 and 50 °C per minute. The decomposition occurred as a two stage process. At 900 °C, complete decomposition occurred leaving 41–46% of a final residue indicating that the final product¹⁸ is Al_2O_3 along with other oxides. If moisture is present, the reaction proceeds as follows:¹⁹

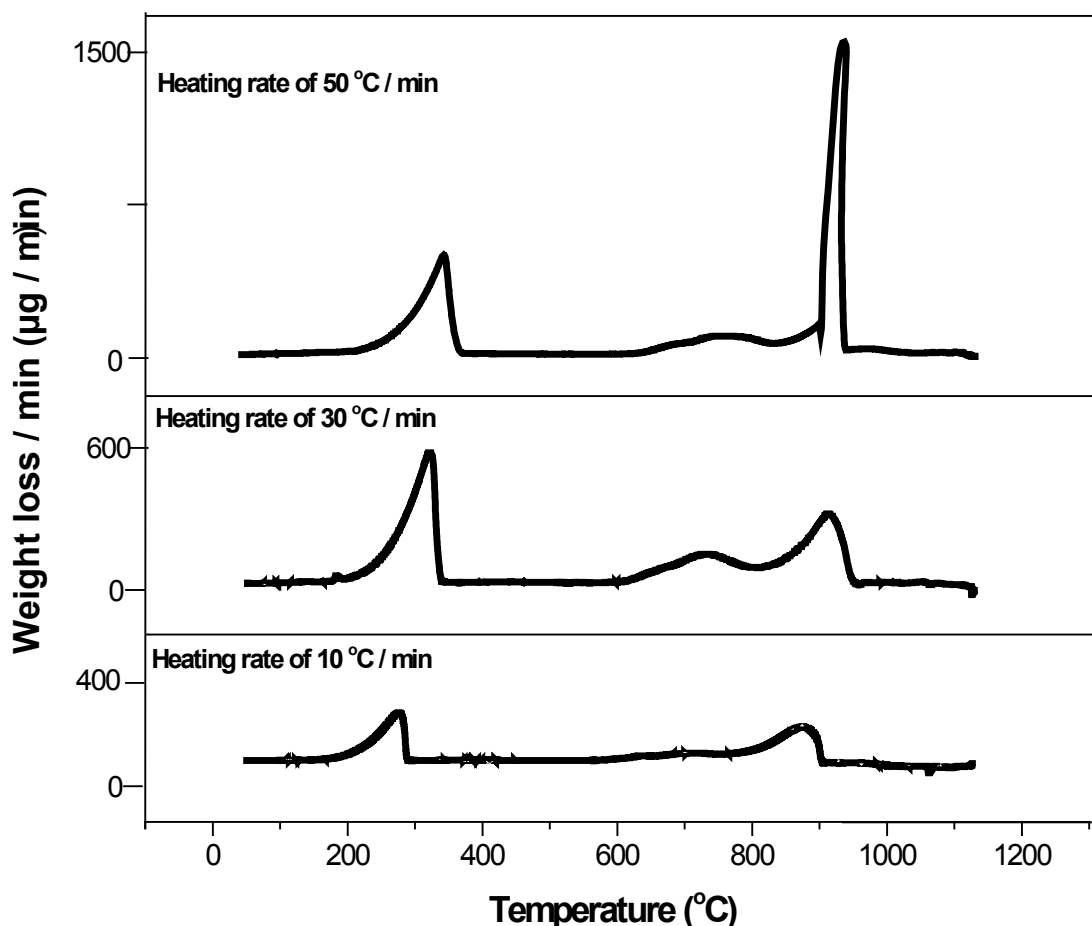
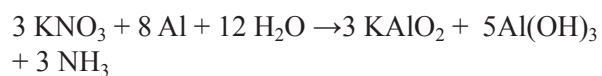


Figure 11. Variation of DTG curve with respect to temperature at different heating rates.



The above reaction might occur evolving heat and NH_3 gas. This reaction is accelerated by the alkaline medium and auto ignition is possible leading to fire accident in the manufacturing unit. A small quantity of a weak acid such as boric acid (H_3BO_3) can effectively retard the decomposition by neutralizing the alkaline products and maintaining a weakly acidic environment. At the relatively slow heating rate of the thermal analysis instrument ($10^\circ\text{C min}^{-1}$), the result indicates approximately a 250°C disparity between the onset decomposition temperature of the pyrotechnic mixtures and oxidizer while the value of the

decomposition temperature of both when slowly heated and when heated at the greater rate showed that the ingredients will decompose at precisely the same temperature (Figure 11). The position of the DTG peak with respect to time varies (Figure 12). Within the firecracker unit, the pressure level varies greatly with time, the fuel would continue to decompose in a low pressure and low temperature environment while the oxidizer component would not fully decompose until the incoming pressure pulse had sufficiently raised the temperature of the reaction front.¹⁹

DSC analysis is used to determine the ignition temperature precisely (Figure 13). There is no overlap of the endothermic peaks and exothermic

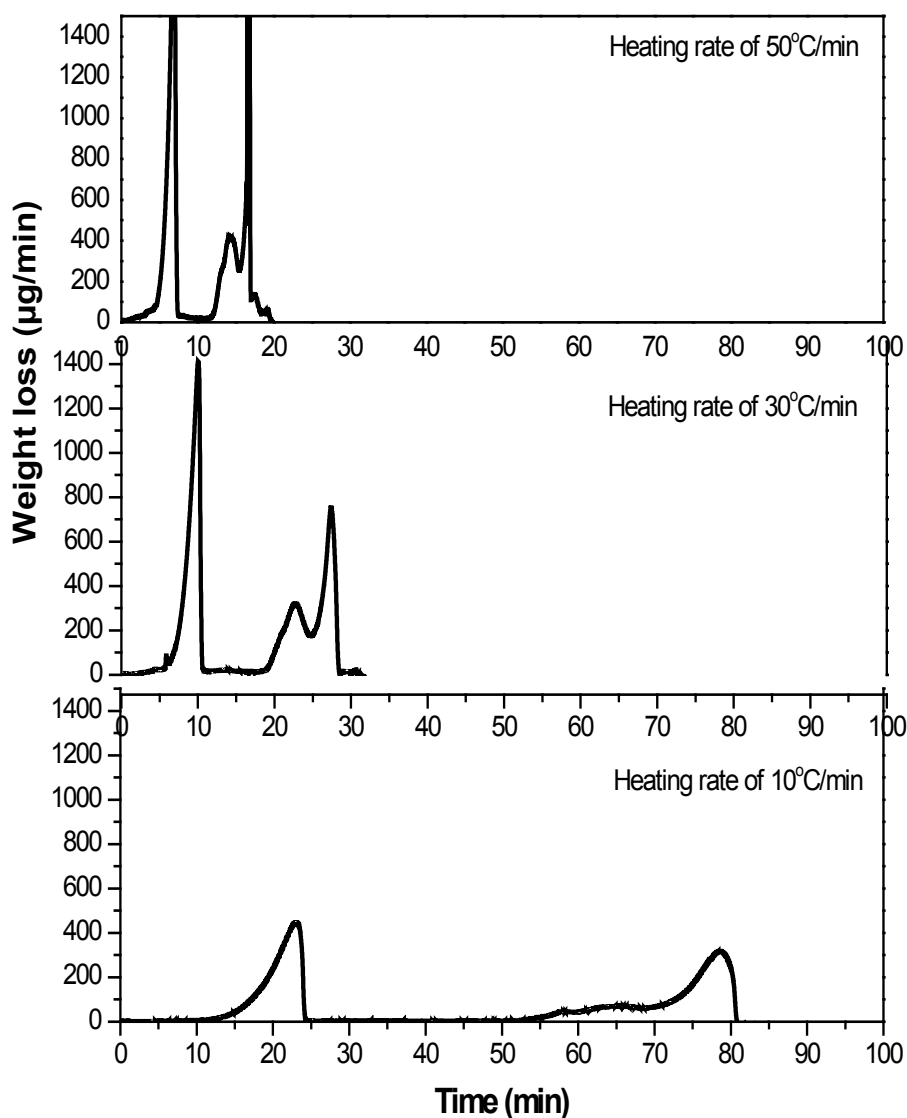


Figure 12. Variation of DTG curve with respect to time at different heating rates.

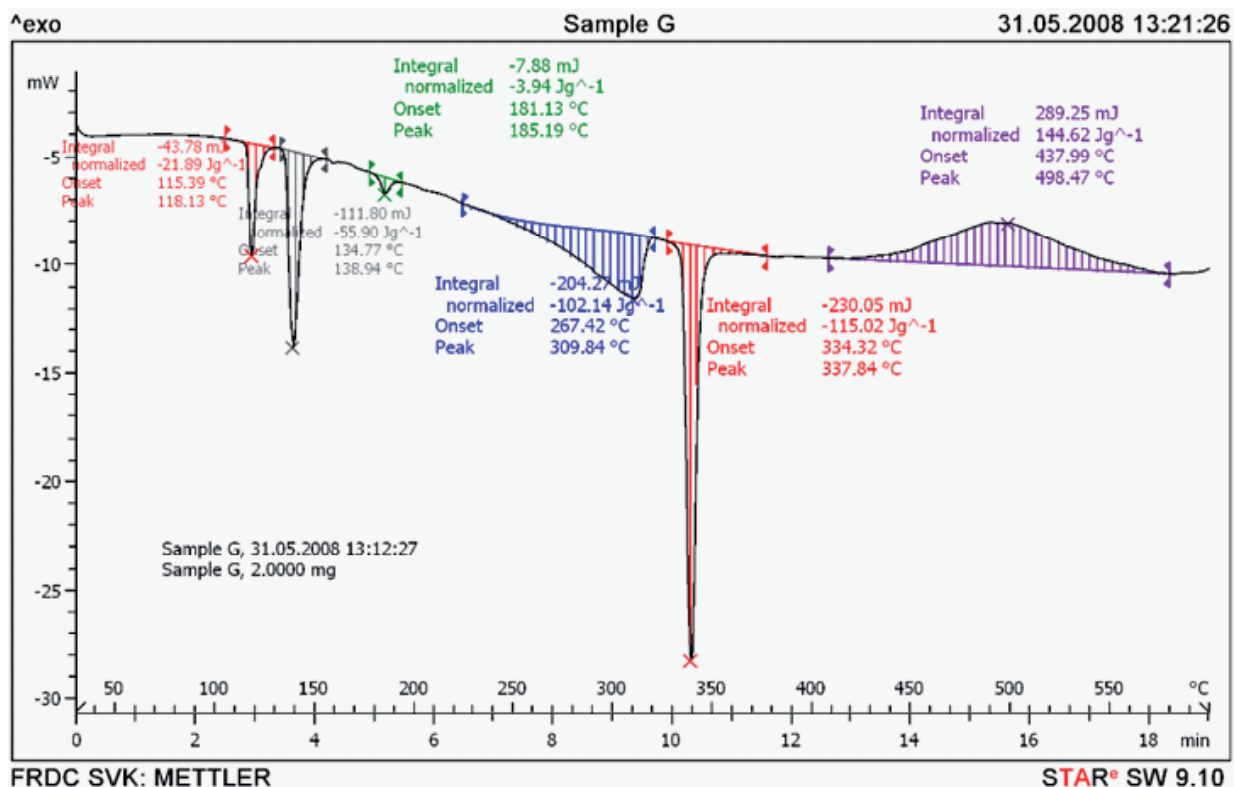


Figure 13. DSC analysis of pyrotechnic mixtures.

peaks. Below 437 °C, there is no exothermic peak and only four endothermic peaks were observed. Among the four endothermic peaks, two sharp peaks correspond to the melting points of sulphur and KNO₃ respectively at 138 °C and at 339 °C. The peaks at 118 °C and 280.5 °C correspond to the phase transitions of sulphur and KNO₃ respectively. DSC analysis (Figure 12) indicates clearly that auto ignition of the mixture, exothermic reaction occurs only above 437.9–498.47 °C indicating the thermal stability of the mixture.

There was wide variation in the composition used among the Indian firework companies though they had to exhibit a specific level of explosivity. Some manufacturers are using unwanted quantities of chemicals. During hazardous situations, the use of excessive quantities of chemicals will lead to excessive damage to the ecosystem. The composition consisting of 57.5% KNO₃, 20% S, 22% Al and 0.5% H₃BO₃ appears to be an ideal composition in all respects with reduced impact sensitivity, required explosivity and allowed sound pressure levels.

Chemistry and mechanism of reaction in firecrackers

The flash composition used in firecrackers consists of an oxidizer, potassium chlorate or barium nitrate with aluminium and sulphur. Sulphur acts as a fuel. When a flash composition is ignited by its fuse, initially, the sulphur melts and the interaction between atoms increases. This results in more atoms with energies exceeding the activation energy that will be in contact and the reaction rate increases with the increasing rate of energy release which leads to thermal runaway at a lower temperature and explosion occurs at a lower temperature. A sharp rise in reaction rate occurs, liberating more heat, raising the temperature further, accelerating the reaction until an explosion occurs or the reactants are consumed. The minimum quantity of the material needed to produce an explosion, under a specified set of conditions, is referred to as the ‘critical mass.’ In a confined system, the hot gases that are produced can build up substantial pressure driving the gases into the high energy mixtures and causing a violent reaction.¹² High explosive reactions produce high sound. The ‘critical mass’

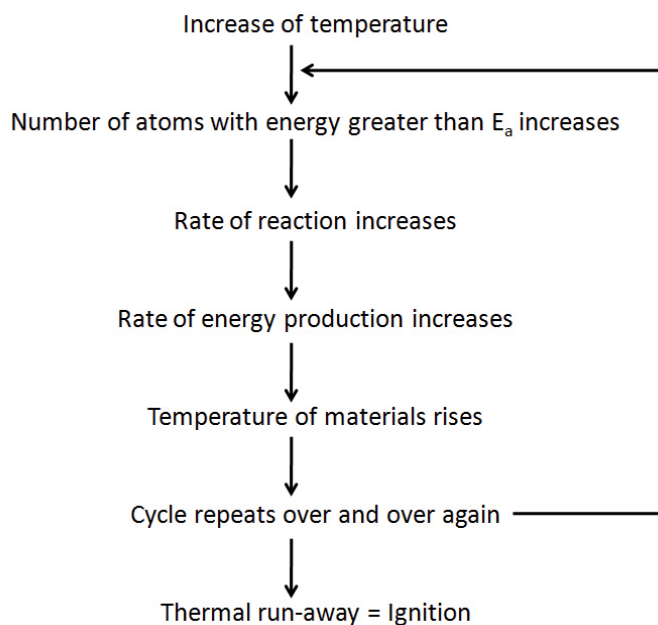


Figure 14. Flow chart for the mechanism of firecrackers.²⁰

should be considered to produce a limited level of sound.

In firecrackers, a different mechanism¹⁴ takes place as shown in the flowchart (Figure 14). The $\text{KNO}_3/\text{S}/\text{Al}(\text{H}_3\text{BO}_3)$ pyrotechnic mixture can be considered as environmentally friendly for making sound-producing crackers compared to the high sensitivity $\text{KClO}_4/\text{S}/\text{Al}(\text{H}_3\text{BO}_3)$ pyrotechnic mixture but the total content of the composition used in the commercial atom-bomb and thunder-bomb can be reduced to produce sound within the allowed limits.

Conclusion

Fireworks are part of social festivals all over the world. It is imperative that use of fireworks does not pollute the atmosphere. Several agencies at national and international levels have imposed restrictions on the safe use of fireworks. In sound-producing firecrackers, the pyrotechnic mixture $\text{KClO}_4/\text{S}/\text{Al}(\text{H}_3\text{BO}_3)$ is not safe for transport due to its high friction and impact sensitiveness. An alternative pyrotechnic mixture, $\text{KNO}_3/\text{S}/\text{Al}(\text{H}_3\text{BO}_3)$, whose inversion temperature is above 400°C and which is less sensitive to mechanical stress is safe for transport. Impact sensitivity analysis indicates that the pyrotechnic compositions studied can be categorized as class III explosives that are sensitive to impact. 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 levels.

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