Impact Sensitiveness Analysis of Pyrotechnic Flash Compositions

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ABSTRACT

Impact sensitiveness of pyrotechnic flash compositions consisting of mixtures of potassium nitrate (KNO_3), sulphur (S) and aluminium (Al) is experimentally analyzed using equipment similar to BAM (fall hammer) equipment. Results indicate that an increase in the sulphur content of the mixture raises its sensitivity to impact. The limiting impact energy (LIE) falls in the range of 5 to 8 J for the compositions studied, which may be categorized as class III explosives. The results obtained, using the statistical tool "Mixture Design", are helpful in correlating the characteristics of each component in the mixture with the overall impact sensitiveness. The model predictions and experimental results are found to match well within $\pm$ 0.5% error. Cost analysis and sound measurements are made for all compositions, and the results are compared with impact sensitivity to arrive at ratios of ideal compositions.

Keywords: flash composition, fireworks, impact sensitiveness, mixture design, pyrotechnics, potassium nitrate, sulphur, aluminum

1 Introduction

Pyrotechnic mixtures are energetic compounds susceptible to explosive degradations on ignition, impact and friction.[1] Several accidents have been reported in Indian fireworks manufacturing units during processing, storage and transportation.[2,3] An analysis of accident data recorded during the past ten years in Tamilnadu in India has shown that the main causes are inadequate knowledge of the thermal, mechanical and electrostatic sensitiveness of fireworks mixtures.[4] Unfortunately, the sensitivity of a mixture to explosion cannot be theoretically predicted as it depends on the reactive nature of the mixture components and the conditions employed during the preparation of the mixture and its handling. Though Material Safety Data Sheets (MSDS) of pure chemicals are readily available, no such data are available for mixtures. Additionally, the mixture's composition varies from company to company for the same type of application. There are no standard procedures or techniques to estimate performance related concepts applicable to mixing ratios. This leads to difficulties in providing a standard scale for assessing the quality of fireworks. Due to the lack of standard manufacturing equipment, tools, manufacturing procedures, combined with a poor understanding of the chemistry of pyrotechnics and their explosive nature, accidents continue to take place in the fireworks industry.

Most fireworks mixtures consist of an oxidizer, a fuel, a color enhancing chemical and a binder.[5] The chemicals employed and their compositions vary depending upon the type of fireworks being produced.[6] The fireworks' effectiveness depends not only on the mixture composition, but also on factors such as particle size, moisture content, packing density and purity of the chemicals.

As per the Indian Explosives Act, 1884, the use of chlorate and sulphur mixtures is prohibited due to its ease of ignition and sensitiveness to undergo explosive decompositions.[7] Alternate mixtures have been widely used in the fireworks industry. Nonetheless, accidents still occur, and the main reason is the poor understanding of the explosive nature and lack of mechanical and thermal sensitivity data for mixtures containing nitrate and sulphur compounds. In the past researchers[8–11] have studied the thermal stability and mechanical sensitivity of sulphur and chlorate mixtures. However, the impact sensitivity of mixtures containing potassium nitrate (KNO_3), sulphur (S), and aluminium (Al) has not yet been reported.

The present study has multiple objectives; the first is the classification of the mixture according to the Andreiev-Beliaev classification of explosivity of substances.[12–13] The other objectives are: to study the impact sensitiveness of mixtures containing KNO_3, S, and Al using the statistical tool "Mixture Design"; to develop a composition with reduced cost and optimum sensitivity that meets the sound levels specified by legislation. The study also assesses the impact sensitivity of flash compositions and helps to choose an ideal composition such that the cost and environmental pollution due to excessive usage of chemicals can be minimized.

2 Chemistry and Mechanism of Flash Composition Fireworks

Flash compositions used in fireworks compositions consist of an oxidizer, commonly potassium chlorate or barium nitrate with aluminum. Some companies use potassium nitrate as the oxidizer, so this paper also examines flash compositions containing potassium nitrate as the oxidizer. Sulphur acts as the ignition source, and aluminum acts as a fuel to oxidize the potassium nitrate. When a flash composition is ignited by its fuse, initially the sulphur melts. During melting, the interaction between atoms increases.[14] This results in more atoms with energies exceeding activation energy that will be in contact and react. As the reaction rate increases, the rate of energy release increases, which leads to thermal runaway at a lower temperature, and the flash composition explodes.

3 Experimental

3.1 Materials

The chemicals used for the preparation of the flash compositions 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 - 91.6%, S - 99.84% and Al - 99.71%. 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.

3.2 Design of Experiments

The statistical tool "Mixture Design" was used to explore the influence of the three components of a flash composition (KNO_3, S, and Al) with regard to sensitiveness. The design of experiments for the mixture design model was generated by the software "Design Experts".[15] Based on the chemistry, as well as currently employed compositions in the industry, the three components were restricted as shown in Table 1. It was understood that the flash compositions had all the components within the specified levels of variation. The limits in Table 1 formed a triangle like that shown in Figure 1 as they were used in the experimental design. This is termed the simplex lattice mixture design model. The three vertices represent the maximum allowed quantity for a specific component. For example, the top vertex represents potassium nitrate with an upper limit of 65%; sulphur and aluminum have limits of 20 and 45%, respectively.

Table 1. Range of Flash Compositions Mixtures.

Component	% Range	
	Minimum	Maximum
KNO_3	50	65
S	5	20
Al	30	45

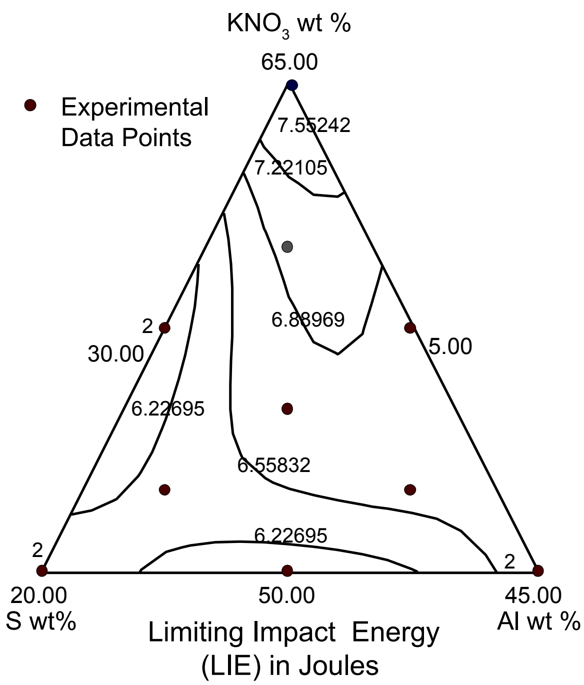

Figure 1. 2-D view of the results for the mixture design showing the results for flash compositions with respect to impact sensitivity.

Table 2 shows the various flash compositions generated by the simplex lattice mixture design model. The experiments were carried out as per the order mentioned in Table 2. In each experiment, 10 g of flash composition was prepared and mixed well, using a wooden spatula in a non-flammable container. The impact sensitiveness measurements were made using the equipment supplied by Electro Ceramics Private Limited, Pune, India as per the procedure described below.

3.3 Measurement of Impact Sensitivity

The diagram of the equipment used in this study for impact sensitiveness measurement is shown in Figure 2. The design and principle of the equipment is similar to that of the drop fall hammer equipment of BAM standards. For each test a 40 mg sample was placed in the anvil and a weight of mass 2 kg (standard weight) was allowed to drop from different heights. The dropping of the weight was controlled remotely. On triggering the remote, the weight fell on the sample through the guides fixed to the column so that the weight dropped directly on the striking head of anvil without rebound and distortion. Ignition of the mixture was observed using an optical sensor. The impact sensitiveness was measured in terms of the Limiting Impact Energy (LIE) and calculated using equation 1.

Table 2. Experimental Data of Flash Composition Mixtures Using the Mixture Design Model.

Exp. No.	Run Order	KNO_3 (wt %)	S (wt %)	Al (wt %)	Drop Mass Height (m)	LIE (J)	Maximum Sound Pressure Level (dB (Al_{max}))	Cost / kg of Mixture in INR
1	14	50	5	45	0.36	7	112	220
2	5	65	5	30	0.41	8.04	114	190.81
3	12	50	20	30	0.34	6.66	115.9	183.32
4	6	50	12.5	37.5	0.3	5.88	114.8	202.07
5	1	57.5	12.5	30	0.31	6.08	114.4	187.07
6	11	57.5	5	37.5	0.34	6.67	110.4	205.82
7	4	60	7.5	32.5	0.33	6.5	113.1	194.57
8	8	52.5	7.5	40	0.37	7.2	115.4	209.57
9	3	52.5	15	32.5	0.31	6.1	112.3	190.82
10	13	55	10	35	0.35	6.8	112	198.32
11	2	65	5	30	0.40	7.88	114	190.81
12	9	50	5	45	0.32	6.27	111.3	220.82
13	7	50	20	30	0.34	6.66	115.2	183.32
14	10	57.5	12.5	30	0.31	6.08	117	187.07

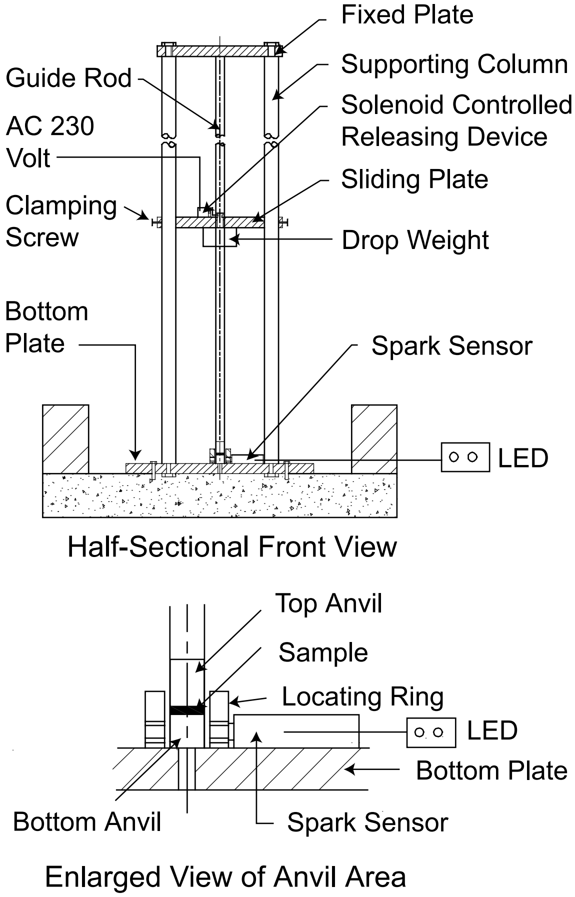

Figure 2. Diagram of the equipment for measuring impact sensitivity.

$$LIE = mgh \qquad (1)$$

where

LIE - limiting impact energy in joules (J)
m - weight of the drop mass in kilograms (kg)
g - acceleration due to gravity (9.81 m/s^2)
h - fall height in meters (m)

The impact sensitivity measurements were carried out according to the procedure outlined in the United Nations (UN) *Recommendations on the Transport of Dangerous Goods*.[16] The UN test procedure recommends BAM (fall hammer) equipment for impact sensitivity measurements. The equipment used in this study was obtained from a local manufacturer, so the validity of the results was tested by matching them with the *LIE* of standard substances.[16] A comparison of the results appears in Table 3. The impact energy measured was within acceptable limits of errors (2–3%). Several runs were undertaken to check the reproducibility of the data.

Table 3. Validity of Test Data for Standardization of the Drop Weight Apparatus.

Substance	*LIE* (J) Tested by BAM (Fall Hammer)	*LIE* (J) Tested by Standardized Equipment	Error (%)
Lead azide (dry)	2.5	2.55	2
Tetryl (dry)	4	4.10	2.5

3.4 Measurement of Sound Level

Sound levels of the flash composition reported in this study were measured using the sound level monitor, Model No. 824 obtained from M/s. Larson-Davis, USA. A test charge of the flash composition was made, and the sound levels were measured according to the specification given in Government of India's gazette notification[17] for sound level measurement. The distance from the sample to the sound meter was 4 m. The test charge (see Figure 3) was approximately 25 mm in length, composed of a three-tier paper board (thickness 1.5 mm). The arrangement was compacted clay at the bottom, about 1.6 g of

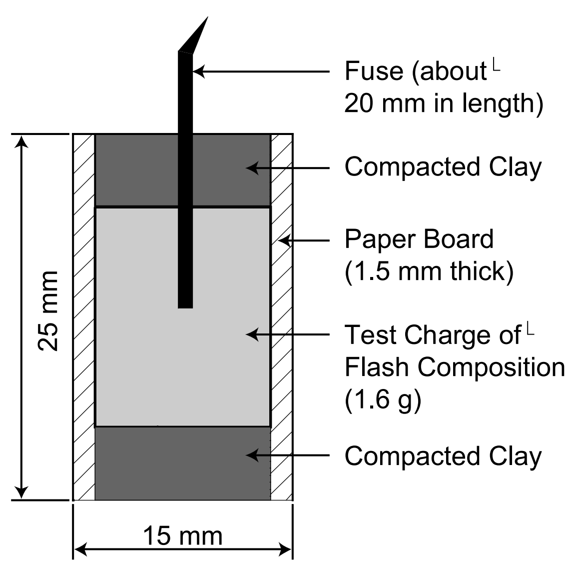

Figure 3. Sketch of test container.

flash composition in the middle, and compacted clay added to the top layer. A fuse (approximately 20 mm in length was placed at the center of the test charge. The results of the maximum sound pressure level in decibels dB (AI_{max}) for each sample are summarized in Table 2.

4 Results and Discussion

4.1 Effect on Impact Sensitiveness

The results of impact sensitiveness measurements for the different flash compositions are given in Table 2. It was observed that the impact energy varied when any one of the component concentrations of the mixture was changed. This behavior was due to the sensitivity and reactivity of each component. A rigorous analysis of the experimental data was carried out employing a simplex lattice mixture design model of Design Experts software. The results are shown in Figures 1 and 4. Figure 1 is the result of the special cubic model fit for the regression of LIE according to equation 2.

$$\begin{aligned} Y = {} & 0.78028\times A + 10.36548\times B \\ & + 1.49537\times C - 0.21396\times A\times B \\ & - 0.042330\times A\times C - 0.33036\times B\times C \\ & + 0.00687\times A\times B\times C \end{aligned} \qquad (2)$$

where

- Y - *LIE* (J)
- A - wt. % of KNO_3
- B - wt. % of S
- C - wt. % of Al

The centroid in the equilateral triangle was considered for discussion of the effects and interaction of each component. The points above the centroid were indicative of less sensitive (higher LIE) mixture compositions while the points below the centroid represented high sensitive (lower LIE) mixture compositions. Varying the quantity of potassium nitrate in the reaction mixture had only a minimal effect on impact sensitivity. However, increasing the concentration of sulphur had a marked influence on impact sensitivity. At lower concentrations of aluminium, the impact sensitivity was greater, but above 40% by weight of aluminium, the mixture became less sensitive. This trend showed that sulphur helped to ignite the reaction mixture rapidly,

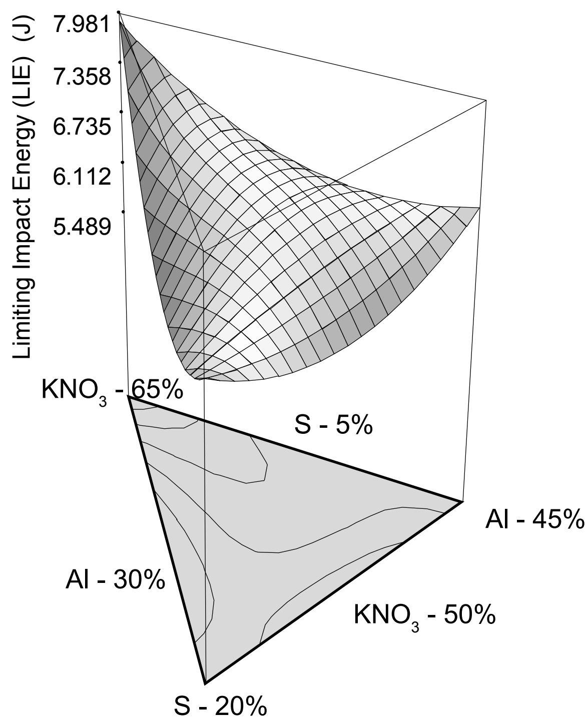

Figure 4. 3-D view of simplex lattice design model mixture contour graph showing the effect and interactions of the flash composition with impact sensitivity.

while aluminum was able to transfer the energy to the oxidizer to a limited level. Further increase in either sulphur or aluminum concentration made the mixture less impact sensitive, and the ability to explode appeared as a limiting factor in the mixture composition. The findings corroborated the previously reported results of sulphur–chlorate–aluminum mixtures.[8–11] This was further confirmed from the statistical model given in equation 2 (i.e., the co-efficient of each element indicated the severity of sensitivity in the mixture).

Moreover there was a narrow distribution of *LIE* (5–8 J) for the mixture ranges studied. Hence the possibility of arriving at optimal mixtures for flash compositions was not raised. From the impact sensitivity results given in Table 2, it was observed that the entire range could be grouped as category III explosives according to the classification of Andreieve-Beliaev.[12–13] Since all the compositions were sensitive to impact, there was no one optimal composition for explosivity. It should also be noted that the explosion effi-

Table 4. Analysis of Variance (ANOVA) for the Special Cubic Model – Partial Sum of Squares.

Source	Sum of Squares	Degrees of Freedom	Mean Square	F value	Prob > F	Remarks
Model	4.581796	6	0.763633	5.419266	0.0216	Significant
Linear Mixture	1.20659	2	0.603295	4.281399	0.0610	
KNO_3/S	2.217775	1	2.217775	15.73886	0.0054	
KNO_3/Al	0.2887	1	0.2887	2.048815	0.1954	
S/Al	0.368433	1	0.368433	2.614655	0.1499	
KNO_3/S/Al	0.500298	1	0.500298	3.550464	0.1015	
Residual	0.986375	7	0.140911			
Lack of Fit	0.707125	3	0.235708	3.376306	0.1352	Not significant
Pure Error	0.27925	4	0.069813			
Corrected Total	5.568171	13				

ciency depends not merely on the flash composition but on the fuse, paper wrap (tube strength) and string wound around the flash composition.

Since the above impact sensitivity results indicated that the entire range of mixtures studied was prone to hazards from impact, all of them also produced good firecrackers. Surprisingly, there was wide variation in the compositions used among the Indian fireworks companies though they had to exhibit a specific level of explosivity. This meant that some manufacturers were employing unwanted quantities of chemicals. During hazardous situations, the use of excessive quantities of chemicals will lead to excessive damage to the ecosphere. Thus, from this study it is possible to arrive at an ideal composition by considering a few other parameters like sound pressure level and cost.

4.2 Sound Levels and Cost Analysis of Flash Compositions

The results of maximum sound pressure level for the flash compositions shown in Table 2 varied within the narrow range from 110 to 117 dB (AI_{max}) when measured at 4 m. The measured ranges all fell below the maximum sound level requirements of 125 dB (AI_{max}) prescribed by the Government of India in a gazette[17] for noise standards for firecrackers. A close look at Table 2, suggests that varying the compositions drastically did not alter the sound pressure level significantly. Thus, the sound pressure level studies prove that a cost effective mixture (within the ranges studied) can be chosen from the point of view of reduced impact hazards and environmenttal pollution. From Table 2 the cost of the compositions varies from INR 183 to 220 for various mixtures that exhibit similar explosivity and hazardous property (impact). Therefore, Composition No. 3 in Table 1 (consisting of 50% KNO_3, 20% S and 30% Al) appears to be an ideal composition in all respects (i.e., reduced impact sensitivity, required explosivity and sound pressure level, and minimum cost).

4.3 Stability of the Model

The stability of the statistical model can be verified from the Analysis of Variance (ANOVA) given in Table 4. The software output shows that the model is significant with probability (P) 0.0216 and no lack of fit with P = 0.1352, which is larger than the reference limit P of 0.005. The normal probability plot of the response residuals is shown in Figure 5. The convergence of the data indicates a minimum deviation from the fit. The goodness of fit (R^2 = 0.82) and the goodness of prediction (Q^2 = 0.67), confirm that the levels are within acceptable limits.[18]

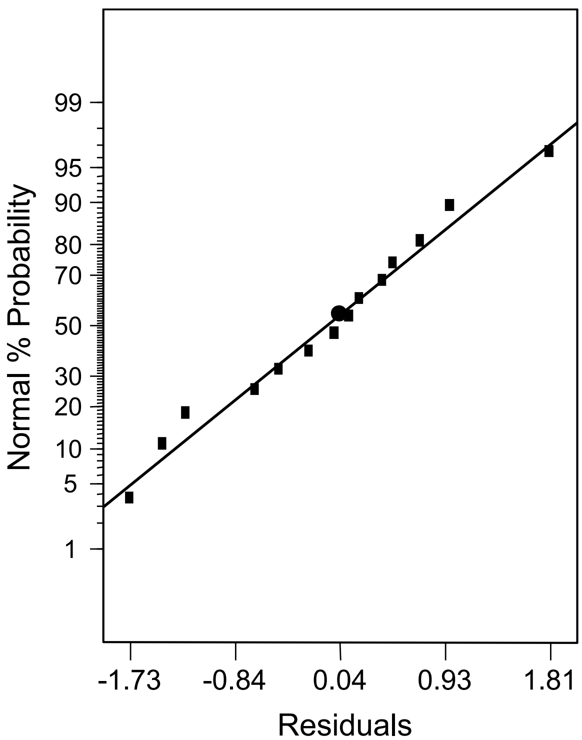

Figure 5. Normal probability plot of the response residues indicating deviation of experiments within the acceptable level.

5 Safety of Flash Composition

The impact sensitivity analysis indicates that the flash compositions studied can be categorized as class III explosives that are sensitive to impact. Hence, caution is required while handling these mixtures.

6 Conclusions

The impact sensitivity measurement studies show that the mixtures are sensitive to impact and can be categorized as class III explosives. The statistical results help to correlate the characteristics of each component in the mixture with respect to impact sensitivity. The model predictions and experimental results are found to match well within a range of ± 0.5% error. The cost and sound pressure level studies suggest an ideal flash composition (50% KNO_3, 20% S and 30% Al) for the fireworks manufacturing industry that has reduced impact sensitivity, meets the specified explosivity and sound pressure level, and has reduced cost.

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