Interrelation Between Impact, Friction And Thermal Energy In A Pyrotechnic Flash Reaction

S. P. Sivapirakasam[a] and M. Surianarayanan[b]*
[a] TIFAC-CORE in Industrial Safety, Department of Mechanical Engineering,
Mepco Schlenk Engineering College, Sivakasi - 626 005, India.
[b] Cell for Industrial Safety & Risk Analysis, Chemical Engineering Department, Central Leather Research Institute,
(Council of Scientific & Industrial Research), Adyar, Chennai - 600 020, India.
* Corresponding author: email: msuri1@vsnl.com

Abstract: *Firework chemical mixtures are sensitive to thermal and mechanical stimuli and lead to many explosive incidents. Experimentally determined thermal and mechanical (impact and friction) sensitivity data of a flash composition mixture are subjected to statistical and graphical analysis in order to understand the mechanism of triggering accidents. The interrelationship study reveals that irrespective of the nature of stimuli, explosion is the final event and occurs due to a thermal mechanism. This study shows that under severe impact thermal stimuli can occur. If the thermal stimuli are equal to or greater than the activation energy of the composition then ignition of the flash composition will occur.*

Keywords: *flash composition, fireworks, mechanical and thermal sensitiveness, correlation analysis*

Introduction

During the firework manufacturing process, chemicals are initially mixed to produce a reasonably homogeneous blend of oxidizer, fuel, colour enhancing chemicals and binders. During these operations impact, friction, spark and heat stimuli may occur, and under certain conditions one or more of these stimuli may be enough to cause ignition of the composition. The sensitivity of the flash composition to these stimuli depends upon the chemical components, purity, particle size, moisture content and packing density. It is therefore extremely important to understand the sensitivity of the chemical mixture to external stimuli.

Studies on thermal stability,[1] impact sensitivity and friction sensitivity[2] of firework compositions have been reported. The reported information cannot be used directly for determining the safety limits for storage, processing, and transportation of firework compositions because no attempts have been made to study the thermal, mechanical and electrostatic hazards together to pinpoint the reasons for accidents to occur. However, in a few reported studies,[3–6] attempts to correlate the mechanical initiation of organic high explosives to kinetics of thermal decompositions are evident.

Ho and Fong[3] compared the impact sensitivity of the various propellants with the thermal decomposition data at 20 ºC min^{-1} and showed that the impact energy had a good correlation with thermal decomposition for the composite propellants with the same binder : oxidizer weight ratio. The results at 20 ºC min^{-1} were used for comparison so as to emphasize the thermal effect most pronounced under rapid heating conditions.

Wenograd[4] suggested that impact sensitivities of organic high explosives were governed by the thermal decomposition processes which took place at the widely varying temperature generated under the impact mass. He found that the temperature at which an explosion would occur within 250 microseconds (a time comparable to the interval under the impact mass) varied greatly among explosives.

Bowden[5] made efforts to study the mechanism of impact initiation. The authors suggested that initiations stemmed from hot spots in the explosive mass generated by a number of possible routes including viscous heating, frictional heating and adiabatic compression of entrapped gases. They concluded that to cause fires in PETN and NG, these hot spots must reach temperatures of at least 430–500 ºC.

Field *et al*.[6] suggested shear banding as a possible source of hot spot formation on impact. In this mechanism, localized plastic flow of material following its structural collapse under compressive stress was related to hot spot formation.

Of all the firework compositions, flash compositions are real explosives that detonate, if a sufficient quantity of powder is present in bulk form, even if unconfined.[2] It is necessary to study the thermal, impact and friction sensitivity of these compositions so that the interrelation and the functioning of mechanical initiation to thermal decomposition can be understood. The work reported here is focused on this objective. Further in this paper, for the first time, Pearson's correlation analysis[7] has been employed to interrelate the mechanical and thermal decomposition parameters and the resulting data have been analyzed using graphical methods.

Experimental

Materials

The chemicals used for the preparation of the flash composition were of commercial grade and obtained from a firework manufacturing company situated in the southern part 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.

The mixture compositions varied in the range of 50–65% potassium nitrate, 5–20% sulphur, and 45–15% aluminum. The range was kept wide so as to cover the range of compositions employed in different fireworks industries in and around Tamilnadu, India.

Thermal studies under isothermal conditions

Intensive studies with the pyrotechnic flash compositions consisting of KNO_3, S and Al were carried out using Differential Scanning Calorimetry (DSC) to analyze their thermal stability and understand the importance of the role of varying proportions and particle size of pyrotechnic flash compositions in inducing cracking characteristics.

DSC module 2910 model (TA Instruments) was used for measurement of thermal stability for the different flash compositions. The studies were conducted with a sample size of 2 mg under pure nitrogen gas at a flow rate of 100 $1 \, min^{-1}$. The equipment and the experimental conditions employed have been reported elsewhere.[1]

Thermal studies under adiabatic conditions

Thermal study of the flash compositions under adiabatic conditions was carried out using an Accelerated Rate Calorimeter (ARC). An ARC 1000 supplied by CSI of Austin, TX was used.[8] About 1 g of sample was loaded into a titanium bomb calorimeter and its temperature raised incrementally by $5 \, ºC \, min^{-1}$ under heat–wait–search mode, until a measurable rate of exothermic activity was detected ($0.02 \, ºC \, min^{-1}$) or the final temperature was attained without any positive thermal input.

Measurement of impact sensitivity

The impact sensitivity measurements of the flash compositions were carried out according to the procedure outlined in the United Nations (UN) Recommendations on the transport of dangerous goods.[9] The design and principle of the equipment were similar to those of a drop fall hammer of BAM standards. The details of the equipment employed have been presented elsewhere.[2]

Measurement of friction sensitivity

The friction sensitivity measurements of the flash compositions were carried out by BAM (friction tester) according to the procedure outlined in the United Nations (UN) Recommendations on the transport of dangerous goods.[10]

Correlation analysis[7]

If two variables vary such that change in one variable affects the change in the other variable, the variables are correlated. The degree of relationship between the variables under consideration is measured through correlation analysis. The measure of correlation is called the correlation coefficient or correlation index. Thus, correlation analysis refers to the techniques used in measuring the closeness of the relationship between the variables. Although there are several methods[11] of analyzing the correlations of physical and chemical sensitiveness, Pearson's coefficient of correlation is simple and highly reliable for measuring the degree of relationship between two variables. The correlation coefficient ρ between two random variables X and Y is given as follows (equation 1):

$$\rho = \frac{n\Sigma XY - \Sigma X \Sigma Y}{(n\Sigma X^2 - (\Sigma X)^2)(n\Sigma Y^2 - (\Sigma Y)^2))^{1/2}} \quad (1)$$

The value of the correlation coefficient ρ always lies between +1 and −1. A value of $\rho = 0$ indicates no correlation. If the value of ρ is near +1 then the variables X and Y are said to be positively correlated and if the value of ρ is near to −1 then the variables X and Y are said to be negatively correlated.

Results

Flash compositions under isothermal conditions

The results of the experiments conducted using DSC for the different flash compositions are presented in Table 1. The DSC plots of the flash compositions for varying sulphur concentration are shown in Figure 1. It can be seen that with increasing sulphur content, the onset temperature

Table 1 *Explosive parameters for the various flash compositions.*

Sample No.	Mixture Components (wt%)			Onset Temperature (ºC)	Peak Temperature (ºC)	ΔH (J g^{-1})	LIE (J)	Friction sensitivity (N)
	KNO_3	S	Al					
1	65	20	15	310.37	319.69	246.2	6.5	360
2	65	17	18	310.68	314.79	253.2	7.9	240
3	65	14	21	313.98	321.79	466.7	7	240
4	65	5	30	305.85	309.37	53.83	7.9	360
5	62	20	18	312.76	321.09	332.1	6	216
6	62	17	21	311.83	320.92	252.5	7.8	216
7	62	14	24	309.85	314.13	56.27	7.2	240
8	62	11	27	308.14	314.02	79.78	8.8	192
9	60	7.5	32.5	304.06	308.14	33.94	6.5	216
10	59	20	21	310.22	314.49	36.24	7.6	216
11	59	17	24	310.5	319.5	358.8	7.6	180
12	59	14	27	303.58	321	966.2	6.1	192
13	56	20	24	312.91	320.5	525.8	6	216
14	56	14	30	306.35	320.3	397.2	6.2	192
15	53	20	27	312.11	313.56	372.3	7.0	216
16	53	17	30	310.37	318.24	409.9	6.3	216
17	53	14	33	311.84	313.88	346	6.4	240
18	53	11	36	310.59	312.87	227.6	6.6	240
19	52.5	7.5	40	307.5	311.2	53.64	7.2	240
20	50	20	30	308.61	319.81	335.6	6.7	216
21	50	17	33	310.97	321.31	534.1	5.9	288
22	50	12.5	37.5	306.75	318.82	367.9	6.0	288
23	50	11	39	311.61	315.3	326.3	6.1	360

Table 2 *Summary of ARC data of flash composition.*

Thermal Inertia (Φ)	Onset Temperature T_o (ºC)	Final Temperature T_f (ºC)	Adiabatic temperature rise ΔT (ºC)	Absolute temperature rise ΔT_{ab} (ºC)	Heat of reaction ΔH_r (J g^{-1})
4.84	191	450	259	1253.6	1311.25

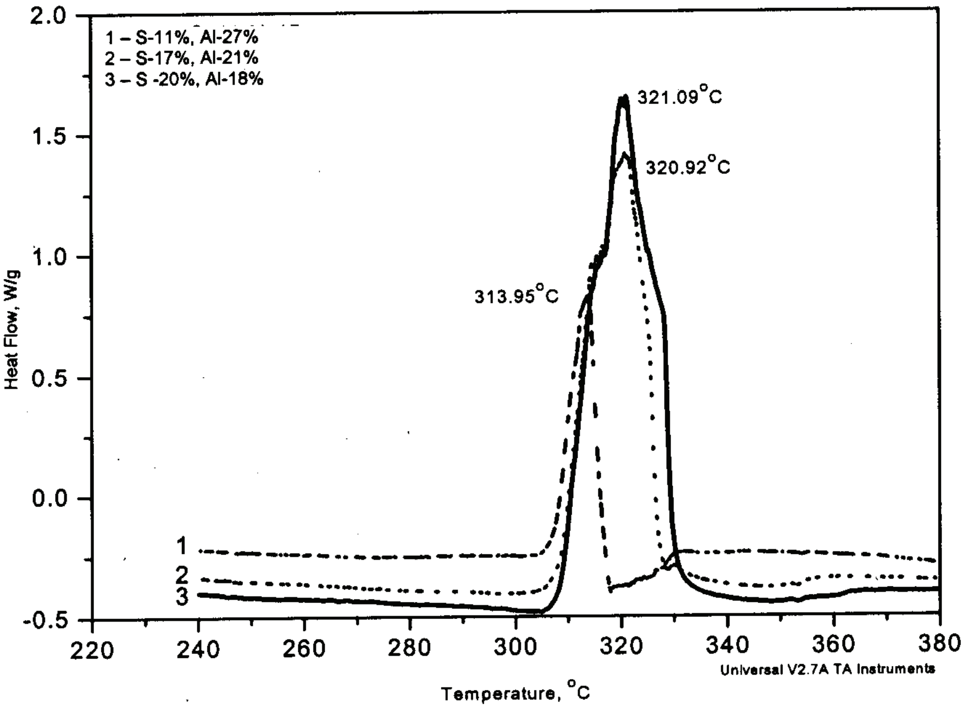

Figure 1 *DSC plots of pyrotechnic flash composition of varying sulphur content (KNO*$_3$*: 62% fixed).*

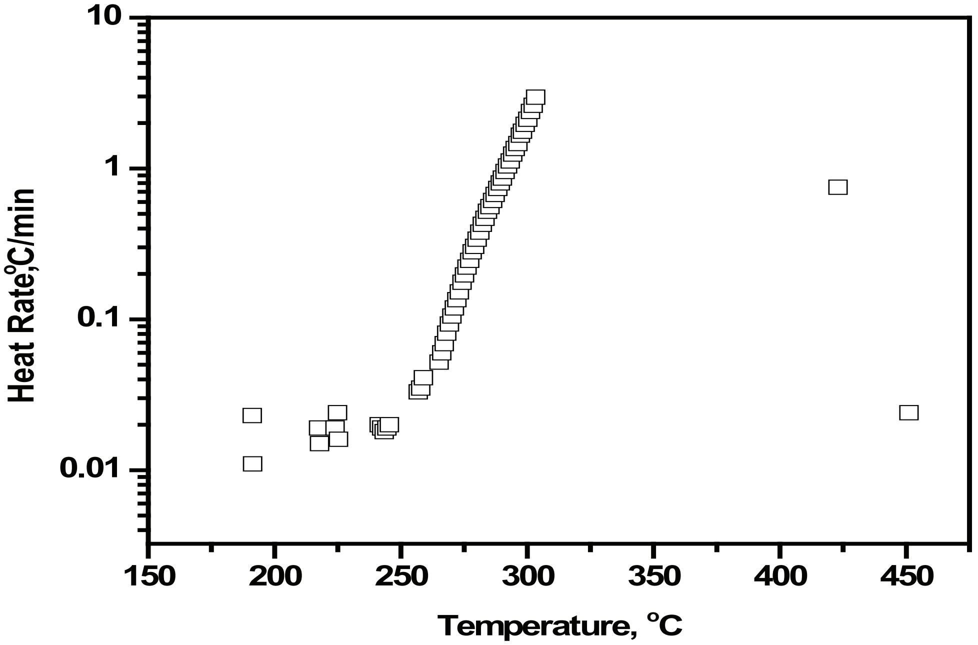

Figure 2 *Self-heat rate vs. temperature plot for thermal decomposition of flash composition (KNO*$_3$ *: S : Al 53 : 17 : 30).*

for exothermic decomposition advances to a higher value to increase the heat of decomposition.

Flash compositions under adiabatic conditions

The self-heat rate plot for thermal decomposition of flash composition consisting of potassium nitrate, sulfur, aluminum in the ratio of 53 : 17 : 30 is shown in Figure 2. ARC data are summarized in Table 2.

Mechanical sensitiveness of flash compositions

The results of mechanical sensitiveness (impact and friction) are shown in Table 1. The limiting Impact Energy (LIE) falls in the range of 5–8 J for the compositions studied, which may be categorized as class III explosives according to the 1965 classification by Andreieve-Beliaev.[2] The friction-limiting load falls in the range of 192–240 N for the compositions studied. The impact energy and friction-limiting load vary when the concentration of any one of the components of the mixture is changed. This behavior is due to the sensitivity and reactivity of each component.

Correlation analysis on mechanical sensitiveness and thermal decomposition

The results of thermal, impact and friction sensitivity data (Table 1) were subjected to Karl Pearson's correlation analysis to understand the

Table 3 *Correlation of mechanical sensitiveness and thermal decomposition parameters.*

Variables	Correlation coefficient	Significance
Limiting impact energy *vs.* onset temperature	+0.26	A weak positive correlation
Limiting impact energy *vs.* peak temperature	−0.6	A strong negative correlation
Limiting impact energy *vs.* heat of reaction	−0.6	A strong negative correlation
Friction sensitivity *vs.* onset temperature	+0.23	A weak positive correlation
Friction sensitivity *vs.* peak temperature	−0.13	A weak negative correlation
Friction sensitivity *vs.* heat of reaction	+0.17	A weak positive correlation

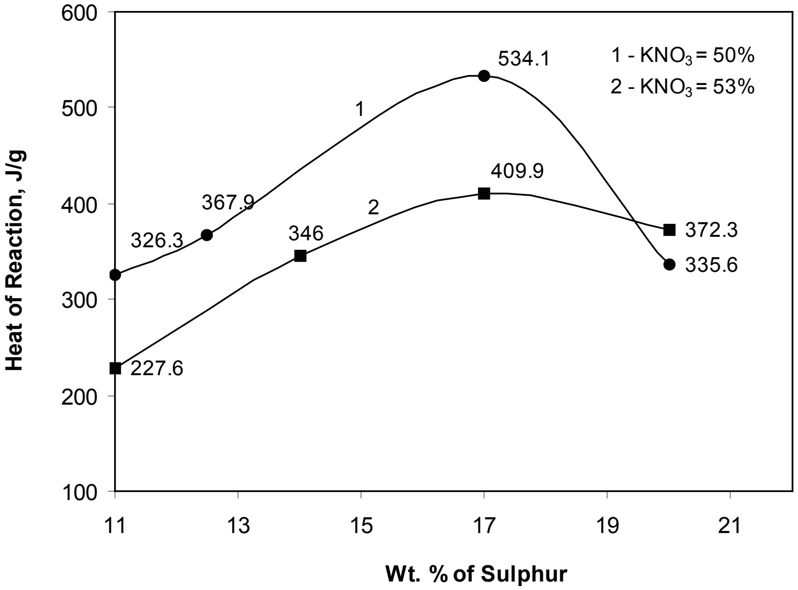

Figure 3 *Effect of sulphur concentration on the heat of decomposition of flash compositions.*

interrelation between the mechanical and thermal explosive sensitiveness.

Equation (1) was employed to determine the correlation coefficient ρ between impact friction and thermal sensitivity. The results are summarized in Table 3.

Discussion

The plot between the decomposition energy and sulphur concentration (Figure 3) showed that with increasing sulphur concentration, the decomposition energy (H decomposition) release increased and reached a maximum value at 17% concentration. Above this, the H decomposition decreased, perhaps due to an increase in concentration of other two components. Table 1 show that the flash composition was found to have explosive characteristics between 11 and 20% of sulphur concentration. Thus, sulphur concentration in the flash composition appeared not only critical, but should also be around the optimum level to exhibit good flash properties. The onset temperature in DSC was above 303 ºC (Table 1). However, the reactive potential of flash composition under adiabatic conditions was severe, and a lower onset for decomposition was recorded as 191 ºC (Table 2). A peak self-heating rate of 2.625 ºC min^{-1} was registered at 302 ºC. The adiabatic temperature rise for the process was 260 ºC. Under adiabatic conditions flash compositions decomposed slowly until 250 ºC (1700 min) (Figure 2), and beyond this the rise in temperature was sudden and sharp. This showed that, under adiabatic conditions, flash composition underwent vigorous decomposition.

Interrelation between limiting impact energy and thermal decomposition

The results of correlation analysis are summarized in Table 3. The strong negative correlation between LIE and ΔH and peak temperature is an indication of the fact that a pyrotechnic mixture, when subjected to an impact force, is triggered to an energetic response *i.e.* it explodes. In Figure 4 the interrelation between LIE and ΔH is graphically shown. It can be seen from the graph that, within the experiments conducted, ΔH increases with the concentration of KNO_3 to a maximum of 59%; between 59 and 62% ΔH drops to its minimum; beyond 62% KNO_3 ΔH increases again. Moreover, with increase in concentration of KNO_3, the impact energy initially decreases and later there is a rapid increase in impact energy before it decreases again. A close examination of the graph reveals that there is an inverse relationship between LIE and ΔH. That is, at lower impact energy (higher sensitivity), ΔH released is higher. This shows that the degree of energetic response is dependent on

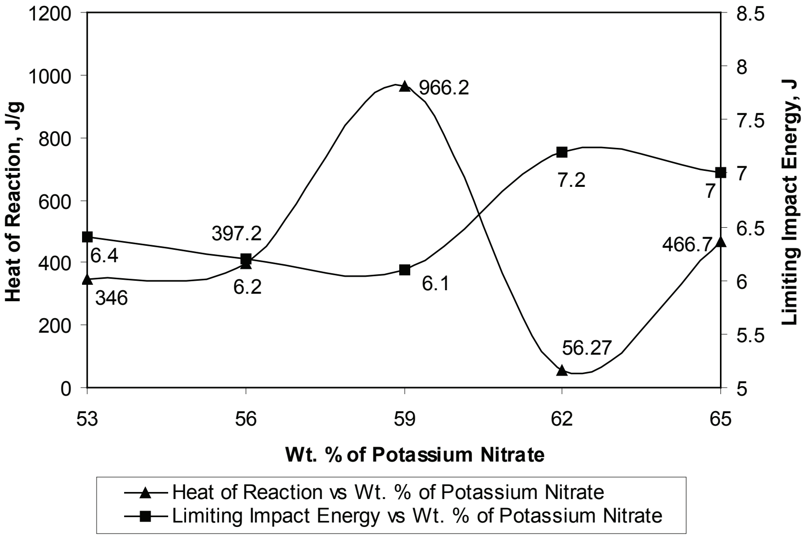

Figure 4 *Interrelation between heat of reaction and impact energy of flash composition at fixed S = 14 wt%.*

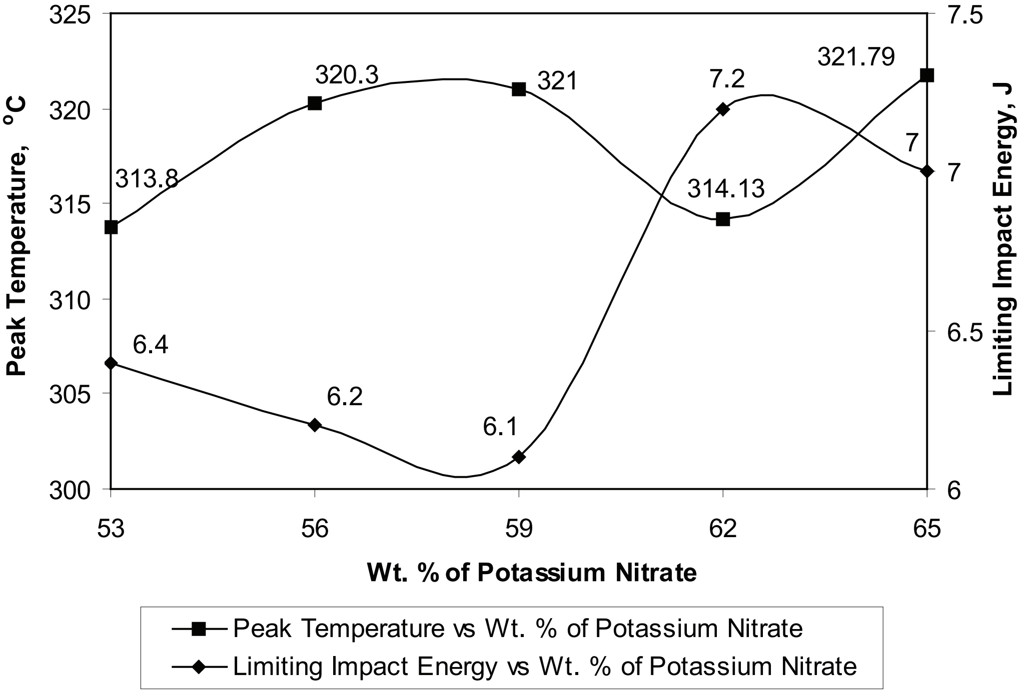

Figure 5 *Interrelation between peak temperature and limiting impact energy of flash composition at fixed S = 14%.*

the concentration of mixture constituents and not the impact force.

In Figure 5, the interrelation between LIE and peak temperature of flash compositions at a fixed sulphur concentration (14 wt%) is graphically shown. It can be seen that higher impact sensitivity leads to higher peak temperature.

From Table 3, the weak positive correlation of the impact energy to onset temperature can be attributed to the fact that the temperature generated through impact energy should be more than that of the onset temperature for the ignition to occur. In the impact sensitivity experimental measurement, the impact energy is measured when the explosion occurs. It is noted that the time factor between the applied impact force and explosion occurring is sudden and almost instantaneous, and may be of the order of microseconds (up to 250 microseconds for most high explosives[4]). In the thermal treatment of the composition under adiabatic conditions, it is seen that sudden and instantaneous explosion is achievable only when the temperature on the mixture is raised to a temperature beyond 302 ºC for the flash compositions (self-heat rate plot Figure 2).

Therefore, it is hypothesized that in impact sensitivity measurement, the temperature generated under impact mass should be more than the temperature of 302 ºC for the sudden and instantaneous explosion to occur. However, this does not mean that explosion will not occur when the impact force produces a temperature lower than 302 ºC (under conditions of less impact). Flash composition is known to undergo a sort of self-heating type of explosive decomposition as observed in the ARC studies. In a practical situation, where the impact force can produce an initial temperature of 191 ºC (development of hot spots) the onset of explosion may occur, however there is some induction time before it reaches the critical temperature of 302 ºC. Therefore, any impact force that contributes to rise in temperature of flash composition around 191 ºC or more is certainly dangerous. Further, the vigor and induction time of the explosion primarily depend on the compactness, density and particle size of the mixture.

There is no direct correlation between thermal and

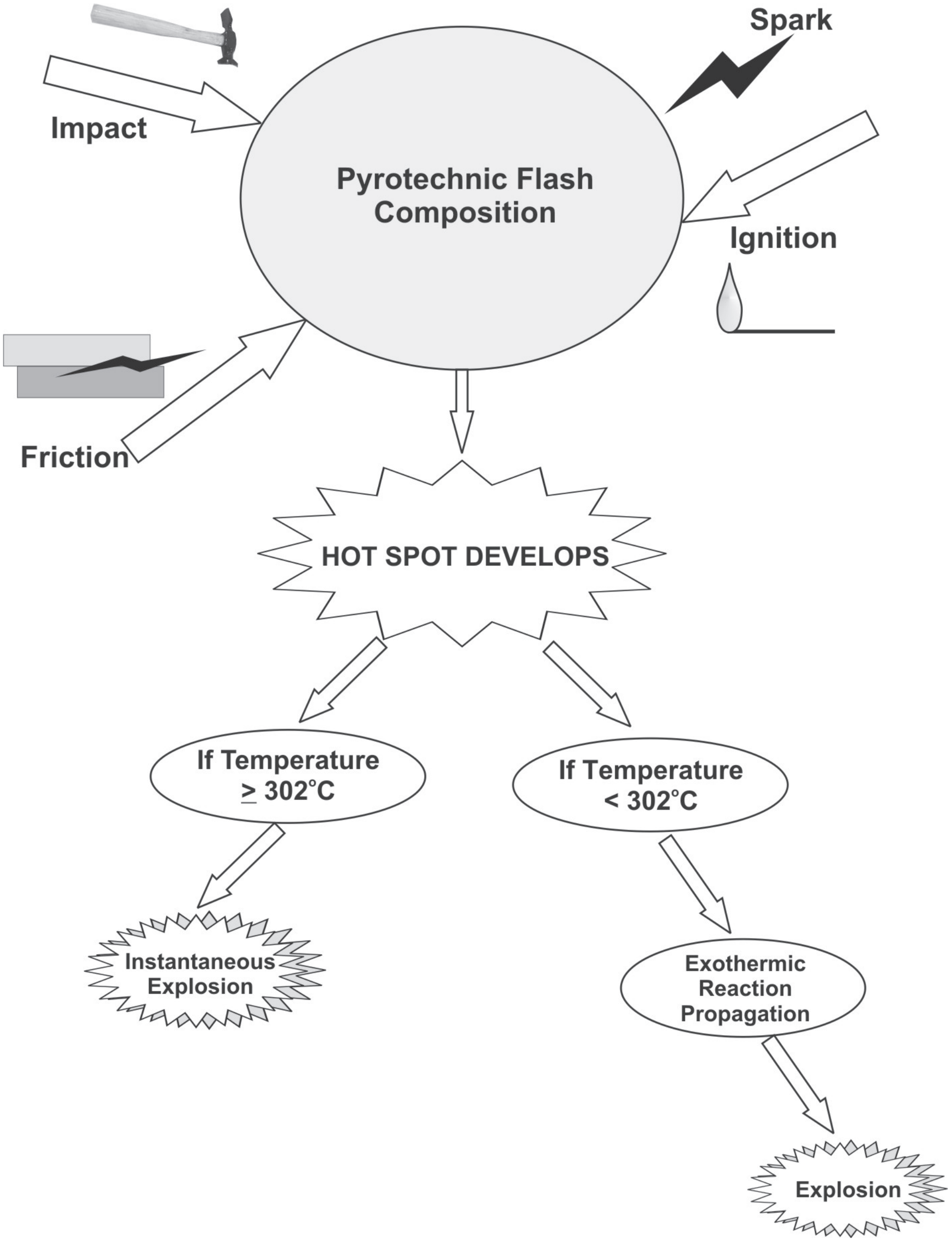

Figure 6 *Flow chart showing the initiation mechanism for explosive decomposition of pyrotechnic flash composition.*

impact sensitiveness, to either predict one from the other or to predict which of these forces can come together to trigger a thermal explosion. It is hypothesized that impact stimuli cause thermal stimuli for the flash composition to undergo thermal explosion. Under severe impact, thermal stimuli can occur immediately and lead to a catastrophic thermal explosion. Irrespective of the nature of the stimulus, explosion occurs through thermal mechanism only. This means that the impact or other kind of stimulus can only initiate the thermal mechanism by providing the minimum threshold energy needed/necessary to a reaction temperature of 191 ºC observed experimentally as the onset point for thermal explosion in ARC. Figure 6 shows the initiation mechanism for explosive decomposition of a pyrotechnic flash composition arising from various stimuli. It is thus possible to interrelate the mechanical form of energy leading to the threshold energy (ΔE) observed in the ARC. This provides a means of suggesting a predictive correlation in such explosive systems. The degree of explosivity also depends on other factors such as compactness, particle size and shape and other environmental conditions.

The impact energy has generally been considered to be insufficient to heat the whole pyrotechnic charge to adiabatic temperature. This may mean that the initiating mechanism is most likely to be manifested under impact pressure due to the following factors:

1. Adiabatic compression of trapped gas.
2. Viscous heating of material rapidly extruded between impacting surfaces or grains.
3. Friction between impacting surfaces, the explosive materials and/or grit particles in the explosive layer.
4. Localized adiabatic shear of the materials during mechanical fail.

Correlation for the flash composition shows that there exists a relation between LIE, Δ*H* and peak temperature. It can be concluded that flash composition mixtures sensitive to impact will also be thermally sensitive and the higher the impact sensitivity, the higher the heat of reaction will be. The degree of energetic response will primarily depend on the mixture compositions and not on impact pressure. A minimum of 302 ºC is required for the instantaneous thermal decomposition under impact pressure for a flash composition. However, any impact force which contributes to a rise in the temperature of flash composition around 191 ºC or more is certainly dangerous. This is because flash composition mixture is known to undergo a self-heating type of explosive decomposition as observed in ARC studies.

Interrelation between friction sensitiveness and thermal decomposition

It can be seen from Table 3 that the friction sensitivity and thermal decomposition are weakly correlated. It is difficult to offer any scientific explanation at this stage; an acceptable reason may be the lack of precision in the measurement of friction sensitiveness. In the BAM friction sensitiveness measurement apparatus (employed in this study) the pyrotechnic mixtures are subjected to a localized frictional load and do not cover the entire sample subjected to the test. Considering the physical nature of the sample and the expected chemical mechanism available for reaction, the friction sensitivity data obtained may not be a true representation of real life situations. Further work is in progress.

Conclusions

The correlation analysis has proved that there exists a relation between impact and thermal sensitiveness for a pyrotechnic flash composition. The inverse relationship between limiting impact energy and heat of reaction shows that the degree of energetic response is dependent on the concentration of mixture constituents and not the impact force. Higher impact sensitivity leads to higher peak temperature during thermal stimuli. The correlation analysis has also predicted that flash composition mixture sensitive to impact will also be thermally sensitive. Further it is hypothesized that impact stimuli cause thermal stimuli for the flash composition to undergo thermal explosion. Under severe impact, thermal stimuli can occur immediately, leading to ignition of compositions. Thus through this correlation analysis, a satisfactory explanation could be projected for an accident triggering mechanism. Further research is required to relate the numerical factors (onset temperature, heat of reaction, limiting impact energy) to gain a thorough understanding of the accident triggering mechanism.

Acknowledgements

S. P. Sivapirakasam is grateful to the management and Principal, Mepco Schlenk Engineering College, Sivakasi, Tamilnadu, India, for their constant encouragement. The author is also grateful to TIFAC, Department of Science Technology, Government of India for offering facilities to carry out this research. The authors are thankful to Mr T. Baskaran, Technician of the Institute, for his assistance while carrying out the impact sensitivity experiments. The authors are thankful to the Head, Chemical Engineering Department and Director, CLRI Chennai, 600020, India, for their kind permission to carry out this study at CLRI.

References

1 S. P. Sivaprakasam, M. Surianarayanan, F. Chandrasekran and G. Swaminathan, “Thermal Hazards of Cracker Mixture using DSC”, *Journal of Thermal Analysis and*

Calorimetry, No. 78, 2004, p. 799.

2 S. P. Sivaprakasam, M. Surianarayanan, G. S. Venkataratnam and P. Nagaraj, “Impact sensitiveness analysis of pyrotechnic flash compositions ”, *Journal of Pyrotechnics*, No. 21, 2005, p. 52.

3 S. Y. Ho and C. W. Fong, “Relationship between impact ignition sensitivity and kinetics of the thermal decomposition of solid propellants”.

4 J.Wenograd, *Transactions of the Faraday Society*, vol. 57, 1961, p. 1612.

5 F. P. Bowden and A. D. Yoffee, *Initiation and growth of explosion in liquid and solids*, Cambridge University Press, Cambridge, 1952.

6 J. E. Field, G. M. Swallowe and S. N. Heavens, “Ignition mechanism of explosives during mechanical deformation”, *Proceedings of the Royal Society of London*, vol. A382, 1982, pp. 231–244.

7 K. Murugesan, *Probability and Statistics and Random Processes*, Anuradha Agencies, p. 54.

8 Y. Iizuka and M. Surianarayanan “Comprehensive Kinetic Model for Adiabatic Decomposition of Di-tert-butyl Peroxide Using BatchCAD”, *Industrial & Engineering Chemistry Research*, vol. 42, No. 13, 2003, pp. 2987–2995.

9 United Nations: Recommendations on the Transport of Dangerous Goods, Test and Criteria, section 21 (BAM Fall Hammer) ST/SG/AC.10/11/Rev. 1, 2nd edn., New York, 1990.

10 United Nations: Recommendations on the Transport of Dangerous Goods, Test and Criteria, Test 3(b) (i): BAM friction apparatus, ST/SG/AC.10/11/Rev. 3, 3rd edn., New York, 1999.

11 S. P. Gupta, *Probability and Statistics for Engineers*.