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Study on nano scale pyrotechnic star chemicals in aerial fireworks manufacturing

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ABSTRACT

Purpose: Firework products are commonly used by people during festival times. Recently people are attracted by aerial display type fireworks because of its mesmeric display performance in the sky. Aerial firework composition consists of various chemicals like aluminium (Al), sulphur (S), potassium nitrate (KNO_3), strontium nitrate, sodium nitrate etc., since these mixtures are hazardous at certain factors like improper mixing of chemicals and presence of moisture, these sources lead to blasting of aerial firework at ground level itself. In normal conventional aerial composition, the usage of chemical is higher and cause more liberation of pollutant in atmosphere. Meanwhile by converting the same composition into nano particles, usage of chemical in aerial fireworks is reduced because of their quick burning rate.

Design/methodology/approach: Ball milling was used for converting all the chemicals into nano particles around 100 nm. Impact sensitivity of the pyrotechnic mixture was tested using the BAM method with an impact sensitivity tester. The friction sensitiveness was determined using a friction tester using the common test methods of BAM25 and corresponded to the UN recommendations on the transport of dangerous goods. DSC and SEM analysis were used as well.

Findings: By reducing the particle size of aerial firework, it reduces environmental damage by reducing the sulphur dioxide, carbon dioxide, carbon monoxide, nitroxide etc., formation by complete combustion of chemicals. The sound and sparkling effect can also be achieved higher than the conventional fireworks.

Practical implications: The quantity of the chemicals used to manufacture the conventional firework composition can be reduced by converting it to the nano size. This reduces the release of pollutant in atmosphere and provides safety to environment.

Keywords: Nano; Micron; Pollution; Aerial fireworks

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MATERIALS

1. Introduction

Fireworks are a class of explosive pyrotechnic devices used for aesthetic, cultural and religious purposes. A fireworks event (also called a fireworks show or pyrotechnics) is a display of the effects produced by firework devices. Fireworks take many forms to produce the four primary effects: noise, light, smoke and floating materials. They may be designed to burn with flames and sparks of many colours, typically red, orange, yellow, green, blue, purple, silver and gold. Fireworks are generally classified as to where they perform, either as a ground or aerial firework (Fig. 1). In the latter case they may provide their own propulsion (skyrocket) or be shot into the air by a mortar (aerial shell).

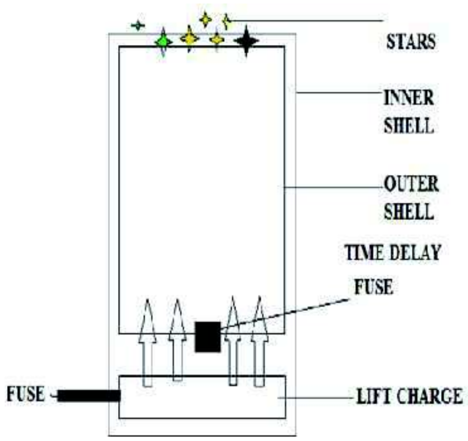

Fig. 1. Schematic view of aerial firework

The most common feature of fireworks is a paper or pasteboard tube or casing filled with the combustible material, often pyrotechnic stars. A number of these tubes or cases are often combined so as to make, when kindled, a great variety of sparkling shapes, often variously coloured. In the pyrotechnic industries, fireworks are manufactured commercially with pyrotechnic chemicals. The chemicals used are oxidizer, fuel and optionally, a colour enhancing chemical and a binder. Pyrotechnic devices, commonly known as fireworks, have a huge popularity. The sonic effect produced by the fireworks mainly depends upon the chemical composition of the mixtures and the particle size. Specifically, this means that larger the particle size, more the quantity of powder mixture is to be used.

Therefore, a high quality product which can produce the expected noise level with lesser quantity of chemicals is a major challenge faced by the pyrotechnic industry. Although there are numerous variations of aerial fireworks construction, the lift and burst charges are propellants usually very similar to black powder (i.e. gun powder), comprised of mixtures of potassium nitrate (KNO_3), charcoal and sulphur. Upon ignition, these materials generate the large quantities of gas needed to propel the rest of the device into the air. The aerial firework powder itself is often in the form of a very fine, silvery-coloured powder, and in this powder form will react very quickly, especially when contained, to generate intense noises and brief, bright flash effects. Reduction of chemicals is the best way to reduce pollution caused by aerial fireworks, but if one does so their performance is compromised. To reduce pollution, lesser amounts of highly reactive chemicals should be used. To improve the reactivity of aerial firework powders, many methods are employed like changing the composition, addition of new chemicals and reducing the particle sizes. In the case of nano chemical powders, if the quantity of the powder is reduced then the release of gas and smoke will be cut down, thereby decreasing environmental pollution without compromising its performance.

This can be achieved by adopting either of the two approaches namely, one, by changing the chemical composition or by changing the particle size. At present the particle size of the chemical composition is at the micron level. However, by converting the composition into nano size, the volume of mixture used will be greatly reduced without compromising the sound level produced. The major advantage of using nano size powders is that it is essentially environmental friendly, producing less pollution and ensuring a cleaner environment.

1.1. Pyrotechnic composition

The pyrotechnic compositions have a wide range of applications utilizing the production of light, heat, sound or smoke and the pyrolants are metal-based pyrotechnic compositions containing virtually any oxidizer. The pyrotechnic compositions used for fireworks are mechanical mixture, which includes oxidant, deoxidizer, adhesive, colorant and other materials with special effects. All the lights, colours and sound of a firework come from these chemicals. An aerial shell is made of gun powder, which is a well-known explosive, and small globs of explosive material called stars. Each star contains four chemicals ingredients: an oxidizing agent, a fuel, a metal-containing colorant, and a binder. In the presence of a flame or a spark, the oxidizing agent and the fuel are involved in chemical reactions that create intense heat and gas. At the centre of the shell is a bursting charge with a fuse on top. Igniting the fuse with a flame or a spark triggers the explosion of the bursting charge and of the entire aerial shell.

The explosion of a firework happens in two steps. The aerial shell is shot into the air, and then it explodes in the air, many feet above the ground. To propel the aerial shell into the air, the shell is placed inside a tube, called a mortar, which is often partially buried in sand or dirt. A lifting charge of gunpowder is present below the shell with a fuse attached to it. When this fuse, called a fast-acting fuse, is ignited with a flame or a spark, the gun powder explodes, creating lots of heat and gas that cause a building of pressure is great enough, and the shell shoots up into the sky. After a few seconds, when the aerial shell is high above the ground, another fuse inside the aerial shell, called a time-delay fuse ignites causing the bursting charge to explode. During the explosion, not only are the gases produces quickly, but they are also hot, and they expand rapidly, accordingly to Charles law, which states that as the temperature of enclosed gas increases, the volume increases, if the pressure is constant. The Table 1 given below gives colorant compounds used in fireworks stars and the colours they produced.

Table 1.
Colorant composition

Colour	Chemical composition
Red	$SrCO_3$+Dextrin+PVC+Mg+Charcoal
Yellow	S+KNO_3(or)$NaNO_3$+Dextrin+PVC+Mg/Al +Charcoal
Green	$Ba(NO_3)_2$ + Dextrin + Mg + PVC
White	S+KNO_3+$Ba(NO_3)_2$+Dextrin +Mg/Al

Pyrotechnic stars usually just called stars which produce intense light when ignited. Stars contain five basic types of ingredients. Fuel which allows star to burn. E.g. – carbon compounds/charcoal powder. Oxidizer which produce oxygen to support the combustion of the fuel. E.g. – potassium nitrate. Colour producing agent. E.g. – strontium nitrate, sodium chloride. Binder which holds the pellets together. E.g. – PVC, red gum.

Pyrotechnic stars are prepared by mixing functional additives such as an oxidizing agent, a fuel, a metal-containing colorant, and a binder in a sieve to have intimate mixture. Then the mixture is granulated to make it easier to handle. In the beginning of the granulation process, core ingredients are slowly rotated in the granulation vessel. A small amount of water is added to the vessel. During this process, the vessel is tilted to keep the movement of the granules inside and to avoid agglomeration. By stirring continuously and constantly adding small amounts of dispersion liquid, the size of the stars gradually increases. After the granulated stars are grown to the required size, they are dried in the closed shed to avoid thermal decomposition due to direct sun ray. After drying in closed shed they are allowed to dry in a drying platform. This drying process takes two to three days. After that aluminium coating is given to each star and allowed to dry for one more day. After drying of aluminium coating charcoal powder coating is given to the stars. Then pyrotechnic stars are assembled in a shell along with lifting charge and igniting fuse.

2. Materials and methods

2.1. Nano technology in explosive

Generally, nanotechnology is the convergence of engineering, leading to the development of structures, devices and systems that have novel functional properties with sizes ranging from 1 and 100 nm. Nanotechnology is emerging as one of the principal areas of investigation that is integrating chemistry and materials science.

While in case of manufacturing the pyrotechnic stars, micron level particles of 250 μ are being used commonly. But in this research work, we have converted into nano level for reducing the environmental pollution and increasing its scintillating effects. All the chemicals used for pyrotechnic star were converted into nano particles around 100 nm. Ball milling was used for converting the pyrotechnic stars.

In the milling process for Barium Nitrate, 35 balls were used and it was conducted over 8 hours duration. The same process for PVC took 9 hours with 35 balls. 35 nm size of very fine aluminium powder was used in this research work and dextrin which is used to bind with the chemicals was directly used.

2.2. Impact sensitivity analysis

Impact sensitivity of the pyrotechnic mixture was tested using the BAM method 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 constant weight of 2 kg was allowed to fall on the chemicals from various heights to find the safest impact energy without ignition.

2.3. Friction sensitivity analysis

The friction sensitiveness was determined using a friction tester using the common test methods of BAM25 and corresponded to the UN recommendations on the transport of dangerous goods. The friction test determines whether a pyrotechnic mixture possesses the danger of explosion or reaction when subjected to the effect of friction. When starting a test with flash powder mixtures, a weight was chosen approximately in the middle of the loading range. If no ignition occurred in six trials, then the load would have to be increased. Friction sensitiveness is a relative measurement reported in Newton (N), when ignition or explosions do not occur even once in six trials.

2.4. Differential scanning calorimeter

Differential scanning calorimetry is a thermos analytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature. Both the sample and reference are maintained at nearly the same temperature throughout the experiment. Generally, the temperature program for a DSC analysis is designed such that the sample holder temperature increases linearly as a function of time. The basic principle underlying this technique is that when the sample undergoes a physical transformation such as phase transitions, more or less heat will need to flow to it than the reference to maintain both at the same temperature. Whether less or more heat must flows to the sample depends on whether the process is exothermic or endothermic. Although the endothermic events result in remarkable data in this work, chiefly we are interested in exothermic behaviour indicative of decomposition.

2.5. Scanning electron microscope

SEM is a type of high-magnification imaging in which the sample is scanned with a focused beam of electrons. These electrons typically interact with the sample material on an atomic level, yielding information about the material's morphology (in the case of the fireworks samples, particle size and heterogeneity). These images are not natively coloured, because no light of visible wavelength is involved. The images are typically shown in black and white. When excited by the electron beam, X-rays characteristic of the atomic composition of the sample are also emitted, which forms the basis of the X-ray elemental analysis. The instrument was run under a relatively high-pressure and humidity environment, enabling imaging of materials sensitive to electrostatic discharge to be performed.

3. Results and discussion

SEM analysis is used to obtain the size of the particle which is processed by ball milling (Fig. 2).

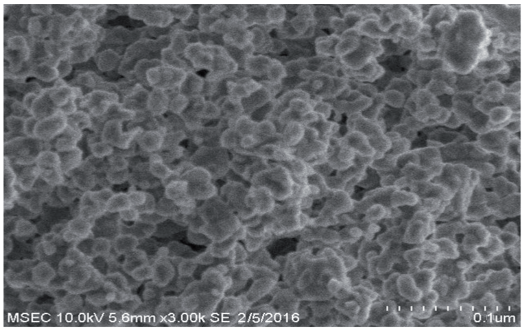

Fig. 2. SEM image of nano composition

Different particle sizes of 250 and 0.1 micron composition samples were taken for the test. Initially, impact and friction tests were conducted to calculate their sensitivity.

In conventional micron size pyrotechnic star composition of 250 microns, the impact energy was found to be 13.73 J. According to UN regulations, the chemicals for which LIE is found to be less than 7.5 J, are considered as very sensitive to impact. So the 250 micron compositions were observed to be safe to handle as the burning rate is low. Comparison of both the results are shown in Table 2.

DSC test is taken for all the samples to find exothermic and endothermic reactions and the results are compared with each other (Tab. 3). Higher the burning rate, quicker was the peak observed in the graph (Figs. 3 and 4).

Table 2.
Comparison of sensitivity test

Result				
Particle size, Micron	250	177	74	0.1
Impact Sensitivity	13.73	12.7	11.77	8.33
Friction Test	Insensitive	Insensitive	Insensitive	Insensitive

Table 3.
Comparison of DSC results

Particle size, Micron	T_{onset}, ºC		T_{peak}, ºC	T_{end}, ºC	ΔH, J/g
64	Exo	214	268	345	346
	Endo	420	432	441	41.16
74	Exo	265	269	277	461.5
	Endo	304	307	310	25.41
0.1	Exo	266	271.6	284.4	486.9

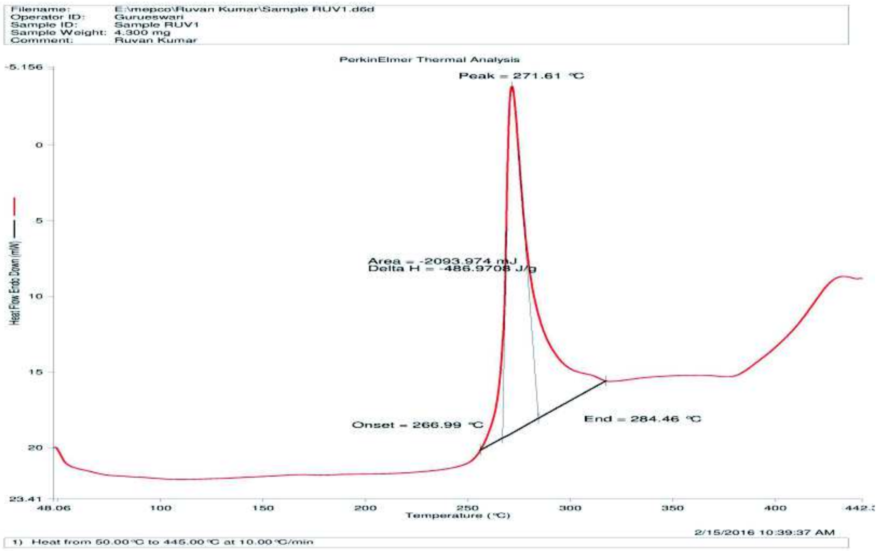

Fig. 3. DSC test result for 0.1 micron

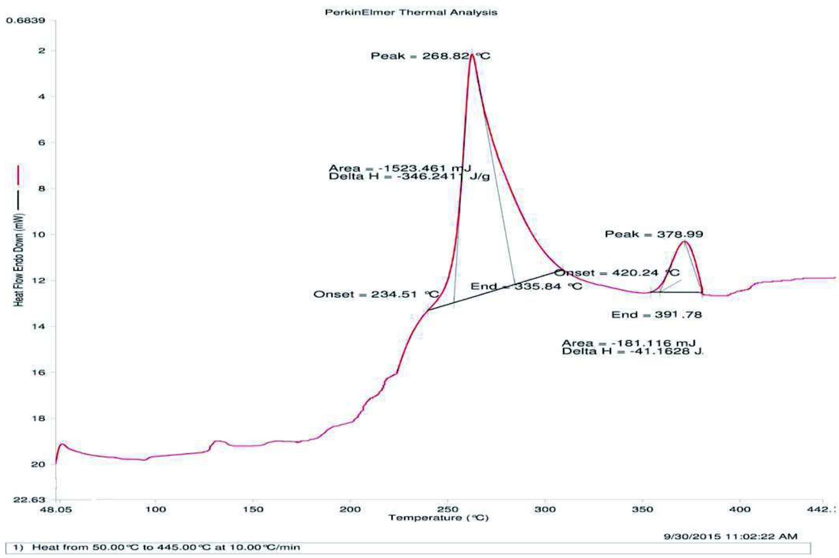

Fig. 4. DSC test result for 64 micron

The heat liberation of nano particle sample is high compared with micron particle size. The heat liberation is increased around 40.74% when compared with micron size particles. Onset temperature is comparatively same for all size of particle. There is a 24% increase of temperature between the 64 micron and 0.1 micron. There is no endothermic reaction present in sample. So from this it can able to conclude that heat liberation is increased when the particle size is decreased.

4. Conclusions

Each pellet of different particle sizes 64, 74, 177, 250 and 0.1 micron were prepared. Impact and friction sensitivity tests were conducted. From these tests, it was observed that there is an increase in sensitivity with respect to decrease in particle size. Thermal analysis showed that quick exothermic reaction would take place when the particle size was decreased and the liberation of heat in exothermic was high when compared with the course sample. From the above tests, it can be concluded that when particle size decreases, the reactivity increases. By comparing all the results an optimized pellet was selected based on safety and scintillating effect.

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