Journal of Scientific & Industrial Research
Vol. 73, July 2014, pp. 479-484

Environment friendly fireworks manufacturing using nano scale flash powder

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Received 20 July 2012; revised 15 November 2013; accepted 30 January 2014

The flash powder composition is used in the fireworks industry to manufacture the firecracker which consists of pottasium nitrate, aluminium and sulphur powder in 75 microns range. During fireworks crackers bursting, more polluted gases are emitted and thus pollute the atmosphere. In this study, synthesis of flash powders and manufactured the fire crackers with the use of nano flash powders. The particle sizes of the chemicals are 139.7 nm for KNO_3, 94.5 nm for Al and 92.36 nm for S. The nano flash powders are mixed with micron powders in different ratios and crackers are manufactured. The residues are collected and analysed for the metal content. Also gas analysis is done for all the combination of crackers. SEM analysis of the residues is analysed. Results shows that crackers made of 100 % nano flash powder provide less quantity of sulphur dioxide and metal content.

Keywords: fireworks, nano flash powders, cake bomb, gas analysis, metal content, mass concentration

Introduction

In fireworks products, to attract the customers, many varieties of chemicals like oxidising agents, fuels, colour producing agents, special effects crating chemicals, substances to produce smoke, binders, phelgmatizers, stabilisers, combustion accelerators / retardants are added[1]. The chemicals used are potassium nitrate, potassium chlorate, potassium per chlorate, sodium oxalate, charcoal, sulphur, manganese, aluminium, iron fillings, aluminium chips, strontium nitrate, barium nitrate, sodium nitrate, calcium carbonate, pitch, dextrin, stearic acid, boric acid, linseed oil, etc. Bursting of fire works cracker results in the release of pollutants like sulphur dioxide, carbon dioxide, carbon monoxide, nitrogen oxides, suspended particles and several metals like aluminium, manganese and cadmium, etc., both as metals and oxides which poses serious health hazards [2].

Fireworks are the unique sources of atmospheric pollution that generate massive quantities of pollutants within a short span of time. During the festivals, like Deepavali and other celebrations in India and abroad, pollutants range in the atmosphere with high ambient concentrations. This leads to climate change and global warming also. Fireworks fallout can contaminate water supplies and residue on the ground. There are many varieties of crackers in Indian market by various manufacturers that giving priority to performance in terms of noise level by adding various chemicals. However, there were no products for which the main focus was to enviro friendly with required performance.

Reduction of chemicals is the best way to reduce the pollution, but if do so; the performance of fireworks could not be achieved. To reduce the pollution, lesser amount of chemicals in the crackers should be used with high reactivity. There are many methods to improve the reactivity of flash powders like changing the composition, addition of new chemicals, and reducing the particle sizes. In case of nano flash powders, the quantity of the powder required to perform the crackers has been reduced and thus the release of gas and smoke will be reduced to a lesser amount, thereby the environmental pollution greatly reduced. In this paper, nanotechnology is applied in pyrotechnic field to improve the reactivity of the flash powders as well as to reduce the environmental impact due to existing firework products.

Teresa Moreno *et al*., conducted the particulate matter measurement during the fireworks event and found that various metal elements presented in the ambient[3,4]. Ying Wang *et al*.,[5] measured the

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particulate measurement during the lantern festival in Beijing and concluded that various air pollutants in the form of polluted gases and particulates are present in the atmospheric air. Some authors conducted the pollution study at the time of festival in India & London and summarised that trace of metal elements like Ba, K and Sr which cause at least 2% increase in non-carcinogenic hazard index associated with Al, Mn and Ba in the exposed population[6,7]. The perchlorate sample was measured as aerosol in the fireworks display during the spring festival which is the main ingredient in the production of fireworks and the results indicated that the level of perchlorate was increased[8]. Many metal traces are emitted during pyrotechnic displays and recognised that, Strontium as the best fireworks tracer during the event[9]. Gerry Croteau *et al*., conducted that study on the emission factors for total particulate matter, metals, inorganic ions, aldehydes and poly aromatic hydrocarbons for pyrotechnics through air sampling in an airtight room after combustion[10]. The pre and post burning analysis of nano aluminized solid rocket propellants was studied by some authors. The post-burning analysis shows the better combustion efficiency for nano-sized aluminized propellants, in comparison with micro-sized and the significant decreases of unburnt aluminium and increases in aluminium oxide among the combustion products[11]. The pyrotechnics residue was analysed by images and observed that confined burning of the flash powders yielded residues whose spheroid particles were mainly comprised of elements from the metal fuel[12]. The post blast of explosives was detected by Fourier transform infrared spectroscopy and found that traces of unreacted explosives were found[13]. Fireworks can create a burst of ozone which is an extremely reactive greenhouse gas molecule that can attack and irritate the lungs. The ozone is believed to be caused by ultraviolet light released by chemicals in fireworks[14]. The nano sized aluminium powder in the flash powder composition show high thermal energy content and high sensitivity for various compositions of flash powder[15].

Many studies have been conducted to study the environmental impact due to the fireworks, but no paper has been found to control the pollution from the fireworks products. Also, unfortunately no research has been conducted to control the environmental impact in terms of particle size of the flash powder composition cracker such as emission of gases, land pollution, health effect during cracker bursting period. Hence, this study will be useful to reduce the pollution to a great extent, contributing to growth and welfare of fireworks industry and society as a whole. In this study, fire crackers made up of flash powder composition which consists of pottasium nitrate (KNO_3), aluminium (Al) and sulphur (S) had been taken.

Cracker preparation

Materials

For this study, KNO_3, Al and S are procured from Sivakasi, Tamilnadu, India, with the particle sizes of – 325 mesh (lower than 75 µm). Then they are sieved in the 40 mesh to remove any impurities, large agglomerated lumps etc. Crackers from open market were procured for comparison study.

Synthesis of nano powders

The aluminium metal powder and sulphur, potassium nitrate powders of various grades is readily available at Sivakasi, Tamilnadu, India. In this study, Fritsch, GmbH, 'Pulverisette 6' planetary mono mill was used for preparing different particle sizes of chemical powder. After grinding the 75-µm sized KNO_3, Al, S & powder for 9 hours in the ball mill, the particle sizes of the output powder were measured by the particle size analyser (Zetasizer Nano ZS, Make: Malvern,UK) and noted as 139, 95 & 92 nm respectively.

Preparation of pyrotechnic mixtures

Various samples of different particle sizes comprising micron and nano sizes with different compositions of flash powder were prepared. The micron flash powder composition was prepared by sieving the chemicals in the 325 mesh (-75 µm) separately and mixed well to get homogeneous mixture. Nano flash powder composition was prepared by using the chemicals of $nKNO_3$, nAl and nS powders. Both micron and nano flash powders has KNO_3: Al: Sin the ratio of 57:23:20which is the prescribed standard composition as per the Government of India norms.The sieves used for this mixing meet the BSS standard. Then, 10 samples are prepared from 100 % nano flash powder to 10 % nano flash powder by retaining the rest as micron size flash powder. The cracker from open market (Refer Table 1 & 2, M1 flash powder) also purchased for comparative testing.

Cracker manufacturing

Cake bomb one of the sound emitting crackers are being manufactured in the fireworks industry. The flash powder composition is filled in the cubic cartoon box and closed by the tissue paper. Gummed jute strings are wound round the box for better confinement. Then fuse wire is inserted in the crackers to facilitate the ignition[16]. The dimensions of the other items are as follows: Inner box dimension: $15 \times 15 \times 15$ mm^3, jute length 0.13 m, winding: 3 ply, GSM 240 g m^{-2}, bursting strength 2.2 kg cm^{-2}.

Experimental and results

Measurement of metal content in the residue

Inductively coupled plasma spectrometer (ICP, Make: M/s. Perkin Elmer Singapore (P) Limited, Singapore, Model: Optima 7000) is a type of spectrometer that is highly sensitive and capable of the determination of a range of a metal and several non-metals at concentrations below one part in 10^{12}. It is based on coupling together inductive coupled plasma as a method of producing ionization with a spectrometer as a method of separating and detecting the metals.

Sample preparation for ICP

The cracker residue sample of 0.1g is accurately weighted in digital balance. The sample is digested with a 1ml of nitric acid (HNO_3) and 3 ml of hydrochloric acid (HCl) solution. The digested solution is completely evaporated to near dryness on a hot plate and then cooled. The residue is dissolved in 2% HNO_3 and make up to 100 ml. Using micro pipette, 1ml of this solution is transferred to standard measuring flask and make up with 2% HNO_3 solution again to 100ml.

Blank & Standard solution preparation

Blank solution refers to 2% HNO_3 solution. This is prepared with the help of millipore water which refers to ultrapure laboratory grade water (Make: ELCA, USA, Option-Q) that has been filtered and purified by reverse osmosis process.1ml standard solution which contains 1mg of metal is taken in standard measuring flask and diluted with 2%HNO_3 and is made up to 100 ml.

Procedure for analysing heavy metals in ICP

Initially blank solution is injected in to the argon gas plasma in the form of mist to trace metal for calibration purpose. Then the probe is transferred in to the standard solution to inject it in to the plasma. The concentration of heavy metals in standard solution is determined. Then the prepared residue samples are introduced by way of a nebulizer which aspirates the sample with high velocity argon, forming a fine mist. The aerosol then passes in to a spray chamber where larger droplets are removed via a drain. The produced droplets are vaporized in the plasma torch and ionized. After atomization, the atoms are excited in hot plasma and emit the wave length. By detecting the emitted wavelength of metals in sample are identified and further their concentrations are determined.

Sample catchers

Sample catcher is fabricated from mild steel to collect the residue after the bursting of fire crackers. It is attached to the walls of a steel cage made and has no resistance to the detonation wave. The size of the sample catcher is about 16 × 16× 15 cm (Banas *et al*., 2009).

Emission gas analysis for the crackers

In the gas analysis measurement, the gas analyser (Model: FEM-55S, Make:Technovation) is used to measure the quantity of SO_2,NO_X, CO, CO_2in the exhaust gas from the burning of flash powder composition. The probe of the gas analyser is inserted in the delivery of the hood which senses the elements and analyses all of the above gases. Fig. 1 shows the value of different gases for the different flash powder composition.

Particulate mass concentration in the air

During cracker bursting, particle concentration in the ambient was measured by using High volume sampler (Make: AMSH product line Pvt. Ltd., Model: PEM-HVF-3). In this instrument, surrounding air is forced to enter into the instrument through filter paper (No: 42) at a flow rate of 2.5 m^3/min. The design of the sampler allows all suspended particle with diameter upto 1.2 µm on the filter paper. Concentration of particulates is determined by measuring the change in weight of the filter paper. In this study, a high volume sampler is kept at the large hall and crackers are bursting in the area. After one hour running an instrument, the filter paper is weighed to find out the suspended particulates concentration.

FTIR analysis

The collected residues are analysed by FTIR analysis to find out the presence of any functional elements of Potassium and Aluminium in the flash powder cracker residue. This result is compared by the pure flash powder chemicals.

From the FTIR graphs, it is clear that the chemicals have two peaks; one in the range of 491-451 cm^{-1} and

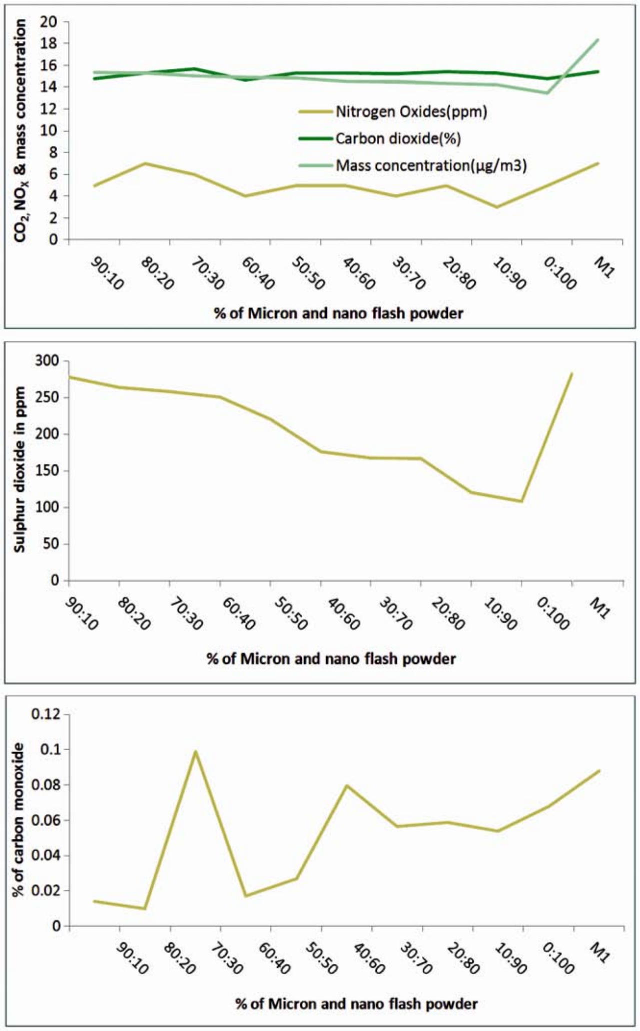

Fig. 1—Gas analysis for the flash powder & suspended particle concentration in air

another in 447.9 - 439.2 cm^{-1} which clearly indicates that these chemicals have Aluminium oxide (Al_2O_3) in the γ-modification (Range 491-451 cm^{-1}) and SO_4 group (K_2SO_4 & $KHSO_4$, range 447.9 - 439.2 cm^{-1}) as asymmetric bond[17,18]. Pure aluminium powder has reacted with oxygen at the time of cracker bursting and hence $Al_2O_3$is noticed in the residue analysis.

SEM analysis

Fig. 2 shows the SEM images of the residues.

Discussion

ICP analysis for the residues of micro and nano flash powder crackers inferred that the crackers made of 100 % nano flash powder has less aluminium and pottasium content in the residue when compared to micron scale cracker residue. This concludes that nano powder has complete combustion attained because of the increased surface area per unit volume which greatly contributes to the high reactivity of nano-sized particles. But in the above results, all residues has some remarkable quantities of metals because of having pottasium bisulphate (K_2SO_4) and Aluminium oxides (Al_2O_3) which are the products of the combustion which is clearly explained in Sec.3.4 using FTIR. The purchased micron sample has the metal content differently because of the unknown composition of chemicals inside the cracker. So, it may conclude that the micron flash powder has more metal content than nano sized flash powder. But there is no correlation between aluminium and potassium content in both micron and nano flash powder crackers residue.

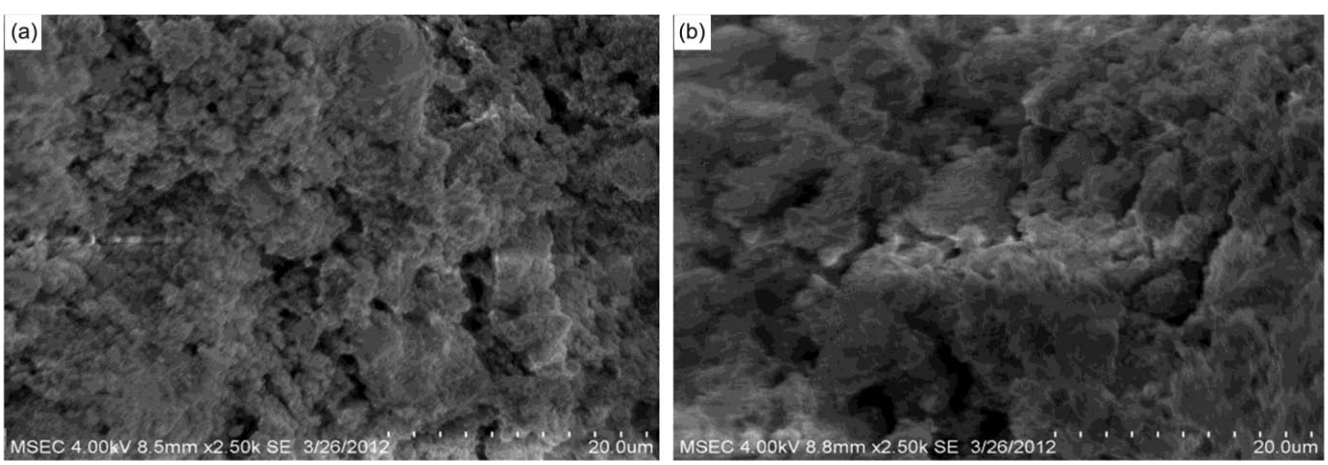

Fig. 2— Residue of nfp cracker (a) 100 % (b) 50 %

From exhaust gas analysis of Figure 1 shows that gases like, NO_X, CO & CO_2 variations are not uniform for different flash mixtures. This may happen because of non-uniform combustion in the confined burning. Thus, it may be deduced that the emitted gas is nearly constant values, irrespective of the particle sizes. But SO_2 emission has gradually reduced with respect to the nano powder addition. This may be because of the more reactivity of nano flash powder. So, the nano flash powder consumes more oxygen quickly and results in the reduction of SO_2 in the emission which is an environmental friendly phenomena, which decreasing the chances for acidic rain[19]. Similarly the other carbon materials present in the fireworks also consumes oxygen results in the non-availability of oxygen for sulphur to form further SO_2.

Fig. 1 further shows that the suspended particulate mass in the adjacent area during the bursting of fire crackers of different flash powder composition. It is inferred that the variation is narrow, because many nano sized particles may be passed through the filter paper which could not be counted.

FTIR analysis inferred that flash powder chemicals of both fresh and post blasting residues have pottasium sulphate and aluminium oxide content. This may be due to oxidation during the synthesis and combustion. So, presence of sulphates and oxide in flash powder after combustion is confirmed.

SEM analyses are used to investigate shape and size of the residues of various crackers. 100 % nfp cracker residue at a large scale (2,500 X magnification) shows different types of irregular agglomerates, formed by primary spherical particles, whose particle diameter is between 1 and 2µm (Fig. 2a). Residues of sample 50 % nfp (Fig. 2b) shows the absence of a nanometric structure of the particles, but with the size of 2 – 5 µm by clustered arrangement.

Conclusion

From the experimentation of flash powders, it is concluded that nano powder has complete combustion because of the increased surface area per unit volume which greatly contributes to the high reactivity of nano-sized particles. Some of the key points are described as below:

- The nano flash powder cracker residue has very less quantity of metal elemental group when compared to micron size flash powder cracker residue. The quantity of aluminium content in the residue is reduced by 81 % for 100 % nfp cracker when compared to 10 % nfp cracker. But there is no change in potassium and also noted that there is no correlation between aluminium and potassium content for the above mixture.
- Moreover decreasing the particle size to nano level, the emission of SO_2 gas also reduces. The quantity of SO_2 gas is reduced by 61 % when burning of 100 % nfp cracker compared to 10 % nfp cracker. Thus the 100 % nano flash powder becomes enviro friendly that reduces the polluted gas emission.
- The FTIR analysis shows cracker residue sample materials have aluminium oxide (Al_2O_3) in the γ-modification and SO_4 group (K_2SO_4& $KHSO_4$) as asymmetric bond.
- The mass concentration of the sampled air is in high range, when the micron size flash crackers bursting.
- The residue of the 100 % nfp cracker shows different types of irregular agglomerates, formed by primary spherical particles, whose particle size is between 1 and 2µm. But it is observed that residue of 50 % nfp shows the absence of a nanometric structure inside spherical particles. This will help to prevent the soil pollution.

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