Ignition and explosion characteristics of four kinds of nanopowders

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Abstract. This work is about the study of ignition sensitivity and the explosion violence characteristics of nanoparticles. It was carried out on various nanopowders as part of a project (NANOGRA) that aims at a multidisciplinary assessment of the risks related to nanoparticles. This paper discusses the experimental results for the determination of ignitability and explosion violence characteristics of Thermal Black N990, Corax N550, MWCNTC7000 and partially passivated metallic nanoparticles (Aluminium). The results of the various tests (MIE, Pmax and KSt) led to the conclusion that carbon nanopowders are capable of generating, when airborne, an ATEX with moderate explosion intensity comparable to the ST1 class. They are little sensitive to electrostatic phenomena. The assessment of explosion parameters of carbon nanopowders was generally found similar to their microscopic size analogue. The pyrophoric nature of partially passivated aluminium nanopowder required screening tests (e.g. MIT layer and combustibility) to control the risk of ignition in the stages of the characterization tests. The results show that aluminium nanoparticles are sensitive to the risk of ignition by a phenomenon of electrostatic origin, and explosion violence seems to decrease when BET specific surface area increases.

1. Introduction

Manufactured nanomaterials are a new class of materials with a huge range of chemical composition, physico-chemical properties and dimensional characteristics. Since they endow the materials in which they are incorporated with some specific physical, chemical or biological properties (robustness, elasticity, adhesion, conductivity, reactivity ...), one has observed a booming interest inside the research community and numerous industrial sectors. However, a substantial number of powdered products are combustible and this very number is expected to increase over the coming years with the advent of surface coated (polymers) nanomaterials which are non-combustible. Many companies that handle powder material are therefore facing a potential dust ignition and explosion risk\cite{1}.

Under certain conditions the clouds of nanoparticles are potentially explosible \cite{2} just like the micro-sized powders, although some differences in pre and post-ignition are suspected \cite{3}. Therefore, the evaluations of the ignitability and explosion violence are essential to minimize the risk of dust explosion. Some research groups have performed tests with various materials to better understand the properties of nano-size powders \cite{4}, \cite{5}. This paper presents some of the measured main explosion safety parameters of multi-walled carbon nanotubes, carbon blacks (Thermal Black N990, Corax N550) and aluminium nanoparticles applied in the course of the NANOGRA project. The parameters for the ignitability and explosion violence of combustible dust are as follows \cite{6}:
• Ignitability: Minimum Ignition Energy (MIE), Minimum Explosible dust Concentration (MEC), not measured and the Minimum Ignition Temperature (MIT) measured only for nano-aluminium;
• Explosion violence: Maximum rate of pressure rise \((dP/dt)_{\text{max}}\) and \(K_{\text{St}}\), Maximum explosion pressure \(P_{\text{max}}\).

2. Tested nanopowders
The experiments were conducted on MWCNT MC7000, Thermal Black N990, Corax N550 and partially passivated nano-aluminium. The specifications of nanopowders used in this study are summarized in Table1. The data come from the suppliers and were not measured by the Laboratory. As expected, the table shows that when the particle size decreases, the specific surface area increases.

| Dust samples          | diameter BET (nm) | BET specific surface area (m²/g) | Supplier               |
|-----------------------|-------------------|---------------------------------|------------------------|
| Thermal Black N990    | 250               | 7 – 12                          | Skyspring Nanomaterials|
| Corax N550            | 62                | 40                              | Skyspring Nanomaterials|
| MWCNT MC 7000         | 10                | 250 – 300                       | Nanocyl                |
| Partially passivated Al | 40 – 60           | 9 – 18                          | Skyspring Nanomaterials|
| Al 100 mm             | 96                | 23                              | -                      |
| (Vignes,2010)         |                   |                                 |                        |
| Al 200 nm             | 210               | 10,5                            | -                      |
| (Vignes,2010)         |                   |                                 |                        |

3. Apparatus and methods
In this study, the explosivity and ignitability parameters investigated for the nanopowders include maximum explosion pressure \(P_{\text{max}}\), size-normalized maximum rate of pressure rise \((dP/dt)_{\text{max}}\), minimum ignition energy \((\text{MIE})\), and minimum ignition temperature \((\text{MIT})\) layer which were measured. European methods were followed using standard test equipment: Anko 20-L explosion vessel (Figure 1), MIKE3 apparatus (Figure 2) and electrically heated circular plate.

The applicable European standards are EN 14034 series (2011), NF EN 13821 (2003) and EN 50281 (2000). At this stage the proposal for “improvements” of test procedure and equipment [2] was not used. The MIE was determined using a modified Hartmann tube (Kühner AG). It consists in a 1.2 L glass cylindrical vessel in which the powders are dispersed and ignited by an electric spark. Both spark energy and dust concentration could be modified to characterize the MIE. The measurements of dust explosion violence, i.e. Pmax (maximum overpressure), and \((dP/dt)_{\text{max}}\) (maximum rate of pressure rise), were performed in a 20 L spherical vessel in accordance with the standard (Figure 1). Explosion violence is quantified by an explosion index \(K_{\text{St}}\) which is defined as
in which we have

P: Pressure, bar
T: Time, s
V: Vessel volume, m³
Kst: Dust explosivity constant, bar.m/s

Regarding aluminium nanopowder (40 - 60 nm), after an incident of self-ignition of the powder during the weighing phases, burning behaviour was investigated by considering the impact of passivation, pre-heating and the preparation procedure. These tests were performed in the INERISS-NANO platform dedicated to the evaluation of nanopowders ignitability and explosivity. They were focused on the evaluation of the nanopowder reactivity and the ignition sensitivity to hot surfaces which constitute one of the main sources of ignition for combustible materials. Once a hot surface has raised the temperature of a portion of powder to its ignition temperature, the combustion reaction self-propagates (from the periphery to the centre of the bulk material).

DSC/TGA tests were performed to characterize the reactivity of the samples and to determine the oxide layer thickness of the particles, which has a direct influence on the thermo-kinetics parameters of aluminium. These results were put in perspective with the data available in the literature to highlight the unique reactivity of this product whose particle size distribution is close to the theoretical critical diameter inducing the pyrophoricity of aluminium. Layer ignition tests, illustrated in Figure 3 and Figure 4, were also performed so that a deposit of dust layer of given size and thickness on a horizontal circular plate was heated to predetermined temperatures until a critical temperature for ignition was reached. Temperature values were ranging between 200 and 450°C.
4. Results and Discussion

4.1. Influence of the specific surface area on the ignition sensitivity and explosion violence.

The main results of this study are summarized in table 2. The results determined in this study were supplemented by those obtained by Vignes [7] for micro size aluminium powders in order to observe the evolution of the parameters as a function of the increase in the specific surface area. According to the results the increase of the specific surface for carbonaceous nanomaterials has no significant effect on the sensitivity to inflammation.

The technical limitation of the Mike3 does not permit to actually determine the MIE level as a function of the nature of the carbon [7]. Usually, for particles in the micron-size range the particle size has a marked effect on the ease of ignition and the explosion violence. The general trend is for explosion violence to increase and ignition energy to decrease [8],[9]. According to the results obtained for the three carbon powders, the increase in the specific surface does not significantly imply an increase in the maximum pressure and in the rate of rise in pressure. These nanopowders can cause an explosion of low severity (explosion class St1). During the explosion test, with lower concentrations range between 60 g/m$^3$ and 500 g/m$^3$, we observed an increase in the values of the explosion pressure whereas with higher concentrations between 750 g/m$^3$ and 1500 g/m$^3$ we observed a decrease in the values of the explosion pressure [7],[6], partly related to the lack of oxidant and some increment of the agglomeration phenomenon. The latter would require further investigation, in addition to some previous studies focusing onto it [10].

| Nanopowders | $P_{\text{max}}$ (bar) | $(dp/dt)_{\text{max}}$ (bar·s$^{-1}$) | $K_{\text{St}}$ (bar·m·s$^{-1}$) | MIE (mJ) |
|-------------|------------------------|-------------------------------------|-------------------------------|----------|
| Thermal Black N990 | 7.2 | 200 | 54 | > 1000 |
| Corax N550 | 7.2 | 242 | 66 | > 1000 |
| MWCNT MC7000 | 7 | 181 | 49 | > 1000 |
| Partially passivated Al 40 – 60 nm | 7.9 | 701 | 190 | < 3 |
| Al 100 nm (Vignes, 2010) | 8.2 | 1340 | 364 | < 1 |
| Al 200 nm (Vignes, 2010) | 9.5 | 2420 | 656 | 7 |
Unlike carbon nanopowders, the increase in the specific surface area of aluminium powders corresponds to a decrease in the MIE (see Table 1 and Table 2). This observation is consistent with the results obtained by [11]. Compared to carbon nanopowders, nanoaluminium can cause significant explosion. However, the values of $P_{\text{max}}$ and $K_{\text{St}}$ obtained are low for this metal nanopowder in comparison to those found in the literature [8]. A decrease in the severity of explosion is noted as the specific surface increases due to the oxidation of aluminium to alumina, which explains the nano Al (40-60 nm) is classified in low explosion severity (St1).

4.2. MIT layer, reactivity and combustibility of passivated nano-aluminium powder.

The aim of these preliminary tests was to assess the risk of ignition in the phases of preparation of the characterization tests and during the cleaning operations in order to secure the test protocol for the future. In addition, it was hoped to get some clues to better understand the mechanisms that drove the inflammation incident at ISSeP during the weighing phase:

During the pre-tests for pyrophoricity, no reaction was observed, which confirms the presence of a coating $\text{Al}_2\text{O}_3$, i.e. partial passivation of the particles. Regarding the reactivity of the product in contact with solvents (water and acetone), after 20 min in the beaker at room temperature, acetone evaporated and no reactivity was noted. For MIT layer, the temperature rose to 292°C at the core of the sample (plate temperature at 400°C), with no noticeable reactivity. Melting of the material and complete oxidation after a TMI with preheating was observed.

During MIT, without preheating and VDI tests, only the surface layer was oxidized. Electrostatic ignition sensitivity test: audible spark when the stick was approached to the disc, but no inflammation occurred. However, this test is not completely conclusive because the energy implemented was less than 3 mJ. An MIE will be performed later. No ignition was observed though the dust layer showed great ignition sensitivity to burning metal particles (sparks) and a differentiated burning behaviour depending on the initial temperature of the powder. It is shown that the initial temperature of the powder has a dramatic influence on the burning class of the nanopowder as confirmed through VDI 2263-1 combustibility tests: at low temperature (<300°C), the aluminium nanopowder burns in a smoldering mode, whereas at higher temperature (>400°C), aluminium burns actively with bright light emission of the burning zone. This type of behaviour, which was observed in the past for some micro-sized powders [12], may have direct implication on the management of fire risks related to deposits of metallic nanopowders, and special attention should be paid to the potential misuse of such test results to set safety barriers.

5. Conclusion

There is a concern that manufactured carbonaceous and metallic nanomaterials might present an ignition and explosion hazard greater that their micron counterparts. This study has shown that for the sensitivity to ignition, two behaviours were observed depending on the nature of the nanopowders. There is a decrease in the oxidation capacity of carbon nanopowders as the specific surface area increases. On the other hand, aluminium nanopowders are more prone to oxidation with the decrease in particle size. Their sensitivity to ignition also increases.

At this stage, researchers have reached some consensus regarding the fact that all the nanopowders tested do not cause a significantly higher explosion violence than that of their microscopic size counterparts. To avoid underestimating the parameter values, and to avoid the phenomenon of oxidation (degradation of the sample), it is recommended that the samples be stored and weighed in an inert atmosphere (under argon) until ignition. At any rate, the samples should not be exposed to the air (oxygen) for long periods of time.
Despite the concerns during the injection of the powders (pre-ignition of the nanopowders and the wall effects of the sphere of 20 l), the evaluation of the parameters of the sensitivity to inflammation and the explosion violence of the nanopowders can be performed with standard devices. Also, the standard methods of evaluating these parameters, intended for microscopic powders, can be applied to nanometric powders by modifying certain steps to avoid degradation of the products before ignition. With the manipulation of nanopowders, reactive and non-reactive, the risk of exposure for operators, of environmental contamination as well as of ignition and explosion require specific attention. Thus the necessity of protective means and measures to reduce and even eliminate the potential risks related to nanoparticles.

As far as protective means are concerned, the individual laboratory protective equipment used at ISSeP is perfectly adapted as it is antistatic (gloves, shoes, overalls).

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