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Explosivity and Flammability of Nanopowders: New Challenges

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Despite a number of studies, the information about the multifaceted dangers associated with the manufacture, transport and storage of nanopowders remains insufficient and justifies the initiative of the NANOGRA project: Nano Global Risk Assessment. The latter aims at a multidisciplinary study (flammability and explosivity, toxicological and eco-toxicological risks) of potential risks related to nanomaterials and nanoparticles with prior economic interest in the Walloon Region. This paper discusses the experimental results of determination of the ignition sensitivity and explosivity characteristics of Carbon Black N990, Corax N550, MWCNT MC 700 and partially passivated metallic nanoparticles (Aluminum). Key information regarding MIE, P_{max} and Kst values was obtained for carbon nanopowders. The results of the different tests have led to the conclusion that the carbon nanopowders are capable of generating an ATEX during suspension in the air, with moderate explosion intensity comparable to the ST1 class. They are little and not even sensitive to electrostatic phenomena. Generally, the assessment of explosion parameters of carbon nanopowders has been found to be similar to their microscopic size analogue. The pyrophoric nature of the partially passivated aluminum nanopowder required screening tests (e.g. MIT layer and combustibility) to control the risk of ignition in the steps of the characterization tests. In addition, against expectations, post-test hazards have been highlighted and required to somewhat adapt some tests protocols. The results show that aluminum nanoparticles are very sensitive to the risk of ignition by a phenomenon of electrostatic origin or self-heating, or friction mechanism event when partially passivated. For some aspects they exhibit expolsivit and flammabilyty risks significantly higher than their microscopic sized “counterparts”l.

1. Introduction

Manufactured nanomaterials are a new class of chemicals with a huge range of chemical composition, physico-chemical properties, and dimensional characteristics. Since they enable to give the materials in which they are incorporated some specific physical, chemical or biological properties (robustness, elasticity, adhesion, conductivity, reactivity ...), one has observed a booming interest inside the research community and many sectors of industry. However a substantial part of powdered products are combustible and this part is expected to increase over the coming years with the advent of surface coated (polymers) nanomaterials, which are otherwise non-combustible. . Many companies that handle powder material are therefore facing a potential risk ignition and explosion of dust (Abbasi, 2007).
The clouds of nanoparticles are potentially explosive (Worsfold and al, 2012) to some extend in the same way as the traditional dusts (microsized powders, although some differences in pre and post-ignition are suspected (Krietsch et al., 2014). 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 (Holbrow and al., 2010), (Vignes et al., 2009). This paper present some of measured main explosion safety parameters of multi-walled carbon nanotubes, carbon blacks (Thermal Black N990, Corax N550) and aluminium nanoparticles performed in course of the NANOGRA project. The parameters for the ignitability and explosion violence of combustible dust are as follows (Eckhoff, 2003):
- Ignitability: Minimum ignition energy (MIE), Minimum explosible dust concentration (MEC), not measured and the minimum ignition temperature (MIT) measured only for nano-aluminum:

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- Explosion violence: Maximum rate of pressure rise (dP/dt)max and KSt), Maximum explosion pressure (Pmax),. Dust explosion is a phenomenon where a flame is propagating in combustible particles cloud dispersed in the air. Therefore, the aforementioned explosion hazard parameters are governed by the flame propagation mechanisms. One of the important steps in the propagation mechanism is gasification of the combustible particles (Dobashi and al, 2006). The particles size (and its distribution) has significant effect on the ignitability and explosion violence because the gasification strongly depends on the particle size. Therefore, these parameters of nanoparticles might be much different from those of the particles of micron scale (Dobashi, 2008).

2. Nanopowders

The experiments were conducted on MWCNT MC 700, Thermal Black N990, Corax N550 and partially passivated nano-aluminum. The specifications of nanopowders used in this study are summarized in Table 1. The data comes from the suppliers and were not measured by the Laboratory. As expected, the table shows that when the particle size decreases, the specific surface increases.

Table 1: Main characteristics of nanopowders

Dust samples	diameter BET (nm)	BET specific surface area (m^2/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 nm	40-60	9 – 18	Skyspring Nanomaterials
Al 100 nm (Vignes, 2010)	96	23	-
Al 200 nm (Vignes, 2010)	210	10,5	-

3. Apparatus and methods

In this study, the explosibility and ignitability parameters investigated for the nanopowders include maximum explosion pressure (Pmax), size-normalized maximum rate of pressure rise (Kst), minimum ignition energy (MIE), and minimum ignition temperature (MIT layer) measured (the latter only for nano-aluminum). European methods were followed using standard test equipment: Anko 20-L explosion vessel, 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 of “improvements” of test procedure and equipment (Krietsh et al., 2013) have not been 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’s energy and dust concentration could be modified to characterize the MIE. The measurements of dust explosion severity, i.e. Pmax (maximum overpressure), and (dP/dt)max, (maximum rate of pressure rise), were performed in a 20 L spherical vessel in accordance with the standard (Figure 1). Explosion severity is quantified by an explosion index Kst which is defined as

$$K_{st} = \left(\frac{dP}{dt}\right)_{\max} \cdot V^{1/3} \quad (1)$$

Where,

P - Pressure, bar
T - Time, s
Vs - Vessel volume, m3
Kst - Dust explosibility constant, bar.m/s

Figure 1: 20 litre sphere ANKO

Figure 2: MIKE3 Kuhner

Regarding aluminum nanopowder (40 – 60 nm), after an incident involving the self-ignition of the powder during the weighing phases, burning behavior was investigating by considering the influence of coating, pre-heating as well as the preparation procedure. These tests were performed in the INERIS S-NANO platform dedicated to the evaluation of flammability and explosivity of nanopowders. They were focused on the evaluation of the reactivity and the ignition sensitivity of the nanopowder to hot surfaces which constitute one of the main sources of ignition of combustible materials. Once a hot surface has raised the temperature of a portion of powder to its ignition temperature, combustion reaction then self-propagates.
DSC/TGA tests were performed to characterize both the reactivity of the samples and determine the oxide layer thickness of the particles, which has a direct influence on the thermo-kinetics parameters of aluminum. These results were put in perspective with data available in the literature to highlight the unique reactivity of this product whose particle size distribution is close of the theoretical critical diameter inducing pyrophoricity of aluminum. Layer ignition tests, illustrated on Figure 3 and Figure 4, were also performed so that a deposit a dust layer of given size and thickness on a horizontal circular plate was heated to predetermined temperatures until a critical temperature for ignition is reached. Temperature values were ranging between 200 and 450°C.

Figure 3: MIT layer test of aluminum (INERIS)

Figure 4: MIT layer test of aluminum (INERIS)

4. Results and Discussion

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

The main results of this study are summarized in table 2. The results determined in this study were supplemented by those obtained by Vignes (Vignes et al, 2010) for micro size aluminum 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. Actually, the technical limitation of the Mike3 does not permit to actually determine the MIE level as a function of the nature of the carbon black (Vignes and al., 2010). Usually, for particles in the micron-size range the particle size has a marked effect on the ease of ignition and the explosion severity. The general trend is for the explosion severity to increase and ignition energy to decrease (Bouillard and al, 2010), (Turkevich and al, 2015). 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 the rate of rise in pressure. These nanopowders can give an explosion of low severity (explosion class St1)..In the lower concentrations range, we observe an increase in the parameters of the explosion severity (Nano Vs micro), while the opposite is observed at higher concentrations (Vignes, 2010), (Eckhoff, 2003), partly related to the lack of oxidant and some increment of phenomenon of agglomeration. The latter would require further investigation, in addition to some previous studies focusing onto it (Murillo et al.2013),

Table 2: Explosion characteristic of nanopowders

Nanopowders	Pmax (bar)	(dp/dt)max (bar·s-1)	Kst (bar·m·s-1)	MIE (mJ)
Thermal black N990	7.2	200	54	> 1000
Corax N550	7.2	242	66	> 1000
MWCNT MC 7000	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 aluminum powders corresponds to a decrease in the MIE. This observation is consistent with the results obtained by (Traoré, 2007) and (Vignes 2007).

Compared to carbon nanopowders, nano Aluminum can cause significant explosion. However, the values of Pmax and Kst obtained are low for this metal nanopowder unlike those found in the literature (Vignes and al, 2010). A decrease in the severity of explosion is noted as the specific surface increases due to the oxidation of aluminum to alumina; which explains the nano Al 40-60 is classified in low explosion severity (St1). This trend is also accentuated by the phenomenon of agglomeration and by pre-ignition phenomenon.

The rate of combustion is reaction controlled unlike nano-aluminum for which it is a function of radiation (Vignes and al, 2010).

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

The aim of these preliminary tests is 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 gain 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 Al2O3, i.e. partial passivation of the particles.
Regarding the reactivity of the product in contact with solvents (water and acetone), after 20 min at room temperature acetone evaporated, in the beaker with water, and no reactivity was noted...
For MIT quantitative layer (not standard), 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 is oxidized
Electrostatic ignition sensitivity test: Audible spark when the stick is approached from the disc, but no inflammation was achieved. 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 however the dust layer showed great ignition sensitivity to burning metal particles (sparks) and a differentiated burning behavior 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 aluminum nanopowder burns in a smoldering mode whereas at higher temperature (>400°C), aluminum burns actively with bright light emission of the burning zone. This type of behavior, which had been observed in the past for some microsized powders (Bartknecht, 1989) may have direct implication on the management of fire risks related to deposits of metallic nanopowders and special attention should be paid on the potential misuse of such test results to design safety barriers.

5. Conclusions

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 is also increasing.
AT this stage, the researchers have reached some consensus regarding the fact that all the nanopowders tested do not have a significantly higher explosion severity than that of their microscopic size counterparts.
To avoid underestimating the parameter values, it might be recommended that the samples are be stored and weighed in an inert atmosphere (under argon) until ignition to avoid the phenomenon of oxidation (degradation of the sample). In any case, the samples should not be exposed for long periods of time to the air (oxygen).
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 severity of the nanopowders can be done 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. The manipulation of nanometric powders, reactive and non-reactive, requires to take into account, on the one hand, the risk of exposure of operators, environmental contamination, ignition and explosion and on the other hand, the establishment of protective means to reduce or eliminate potential risks related to nanoparticles.
The individual laboratory protective equipment used at ISSEP (gloves, shoes, overalls) is antistatic. However, ignition of the powder by electrostatic spark cannot be totally ruled out. The floor and the over-shoes may have conductivity defects. If the over-shoes are made of the same material as the disposable coverall, they cannot guarantee a good dissipation of electrostatic charges. Following a second spontaneous ignition event during tests, the mechanism of friction must also be considered as a possible origin of this phenomenon.

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