

EXPLOSION PROPERTIES OF NANOPOWDERS[†]

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INTRODUCTION

Nanotechnology is a rapidly expanding technology in which existing and novel materials are engineered at the nanoscale. Engineered nanomaterials include uniquely manufactured products with unique shapes and enhanced physical and chemical properties, compared with conventional materials of the same composition.

There is currently little available information on the explosion risks of nanoparticles. The little data that does exist is contradictory and suggests the explosion violence is less than that of larger particles, which goes against the expectation that smaller particles burn faster than larger ones due to the increased surface area.

Fine powders are known to be an explosion risk, particularly organic and metallic powders.

For fine particulates, there is standard test equipment available to determine the explosion and ignition characteristics for powders, but these typically require kilogram quantities of powder. Also, the powder is dispersed in the standard apparatus using compressed air. With nano-powders, their large surface to volume ratio means that many are spontaneously flammable on contact with air, or surface oxidation alters their properties. Hence equipment that avoids oxidation until the point of ignition is required.

A research project has been commissioned by HSE and was partly funded by the HSL Internal Research Programme to explore the explosion and ignition behaviour of nanopowders. The aim of the project is to develop equipment and techniques and to measure the explosion and ignition characteristics of nanopowders.

During this project specialised equipment has been developed and existing equipment modified to enable the assessment of a range of nanopowders including metal and organic nanopowders. This paper presents the equipment developed, the techniques used and results obtained to date.

EXPLOSION SEVERITY TEST APPARATUS

The procedure for measuring the explosion severity of dust/air mixtures is described in a European standard available as BS EN 14034-1 (2004) and BS EN 14034-2 (2006). The standard test vessel for these determinations is the 1 m³ vessel.

The peak maximum explosion pressure, P_{\max} , and the peak maximum rate of pressure rise, $(dP/dt)_{\max}$, are measured in this standard test procedure. The P_{\max} and $(dP/dt)_{\max}$ are the highest values generated in an enclosed dust explosion. These characteristics are measured in a standard test at the optimum dust concentration and are obtained by testing the dust over a wide range of dust concentrations. The two

peaks normally occur at different dust concentrations. The $(dP/dt)_{\max}$ is used to calculate a dust specific explosibility characteristic called the K_{St} value. The K_{St} is given by:

$$K_{St} = (dP/dt)_{\max} V^{1/3} \quad (1)$$

Where $(dP/dt)_{\max}$ is the peak maximum rate of pressure rise (bar/s) and V is the total internal volume of the test vessel (m³). The units of K_{St} are bar m/s.

Equation (1) is well known as the “cubic law” (Barton (2002)). The K_{St} is considered to be a constant for any dust, independent of vessel size and equation (2.1) acts as a simple scaling law. The K_{St} value is derived only from measurements in either a 20 litre sphere vessel or a 1 m³ vessel and if any other vessel is used to measure the K_{St} it must be calibrated against the 1 m³ or 20 litre standard test vessels.

The powder is dispersed in the standard apparatus using compressed air. With nano-powders, their large surface to volume ratio means that many are spontaneously flammable on contact with air, or surface oxidation alters their properties. Hence equipment that avoids oxidation until the point of ignition is required. Also, the standard test equipment typically requires kilogram quantities of powder, hence this scale of testing is not viable due to the economics and the limited availability of material.

No commercial equipment is available to satisfy these requirements, so equipment has been developed to measure the explosion characteristics of nanopowders.

TEST VESSEL

An explosion test vessel (Figure 1) has been designed and manufactured specifically for testing nanopowders. The vessel has a spherical test chamber and an internal volume of 2 litres.

The test vessel is connected to auxiliary systems to deal safely with the handling and disposal of nanopowders.

PORTS

A number of ports and flanged connections are incorporated to accommodate electrodes for the dust ignition, pressure transducers, glass viewing window, dust injection port, pressure relief and evacuation port.

DUST INJECTION

Dust injection is achieved using a fast-acting valve and solenoid system mounted at the base of the vessel.

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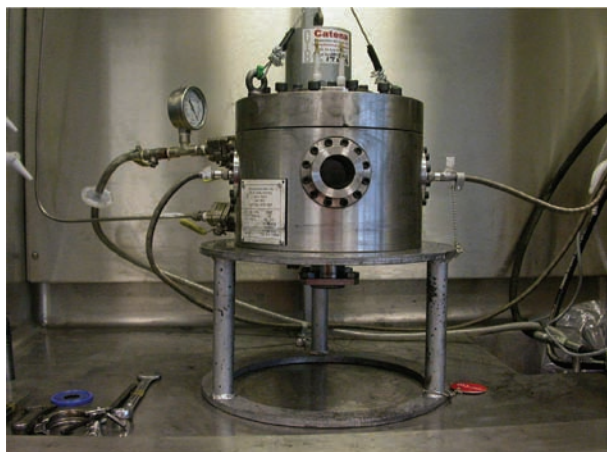


Figure 1. 2 litre test vessel

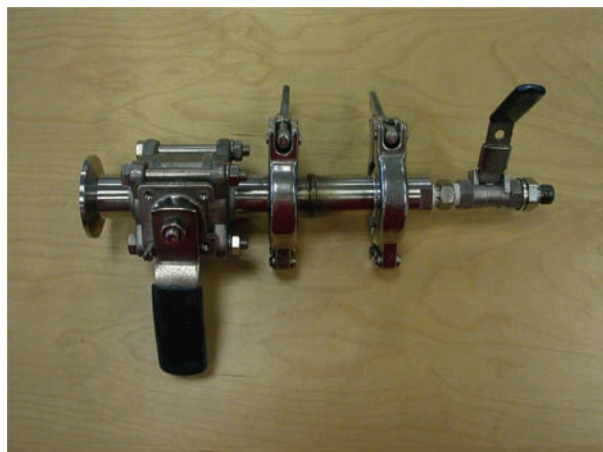


Figure 3. Dust container

NOZZLE

Three dust distribution nozzle designs were considered (Figure 2) A pepper-pot nozzle was selected for the test programme.

DUST CONTAINER

A special dust container (Figure 3), designed for a working pressure of 20 bar, is attached to the dust injector. It is designed to enable nanopowder can be loaded and sealed within the dust container under an inert atmosphere.

IGNITION

Ignition of the dust cloud is achieved using an ignition source located in the centre of the test vessel.

MINIMUM IGNITION ENERGY TEST APPARATUS

The MIKE3 test apparatus, manufactured by Kuhner is normally used for the determination of minimum ignition energy (MIE) of micron-sized dusts. However, the risk assessment for handling nanopowders required improvements to the operating procedure for this apparatus. This equipment was therefore modified to minimise operator contact with nanopowders and enable the safe handling, and loading of the powder into the apparatus.

DUST DISPERSION CHAMBER

A two-stage process was used to develop the modified dispersion chamber.

Development Stage 1: An enclosed barrel shaped chamber was constructed to completely replace the Kuhner dispersion cup assembly (Figure 4).

This comprised a stainless steel chamber split into three components, lower middle and top barrels that were



Figure 2. Dispersion nozzles

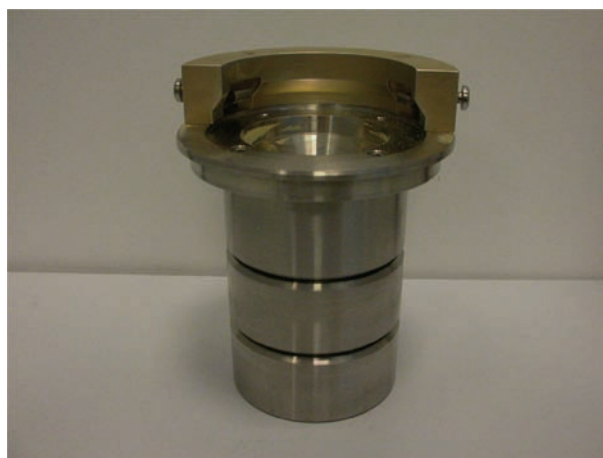


Figure 4. Dispersion chamber

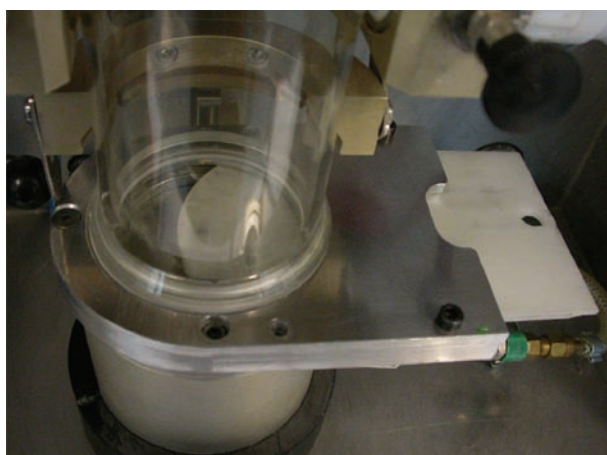


Figure 5. Slide valve dispersion chamber

screwed together to form the assembled chamber. Two aluminium bursting discs were sandwiched between the barrels to form a central chamber that held the nanopowder.

Development Stage 2: A second dispersion system was developed utilising the existing Kuhner dispersion cup. A thin slide valve was manufactured and fitted to the top face of the dispersion cup (Figure 5). The close fitting of the slider and fixed slides provided a sealed chamber once the valve was closed and allows nanopowder to be loaded and sealed under an inert atmosphere. This design was used for the main test programme.

TEST MATERIALS

A range of nanopowder test material were used in the test programme and are listed in Table 1.

TEST RESULTS

COMMISSIONING TESTS

Initial commissioning was done using micron-scale lycopodium powder and aluminium nanopowder (Table 2). The maximum rate of pressure rise and maximum explosion

Table 1. Nanopowder test materials

Nano powder	Sample number	Supplier	Information from supplier
Aluminium	EC/104/08	Intrinsic	Nominally 100 nm QNA2607
Aluminium	EC/011/09	Intrinsic	Nominally 210 nm QNA2798
Multi-walled carbon nanotubes	EC/153/07	Nanostructured and Amorphous Materials Inc.	MWNT Purity: > 95%; Outside diameter: 20–30 nm; Inside diameter: 5–10 nm; Length: 10–30 um; SSA: ~ 110 m ² /g; Colour: black; True density: ~2.1 g/cm ³
Carbon nanofibre	EC/042/08	Pyrograph Products Inc	Diameter 100–200 nm Length 30–100 micron
Carbon nanofibres	EC/158/07	Nanostructured and Amorphous Materials Inc.	Carbon nanofibers; Purity 95%; Outside diameter: 80–200 nm; Core diameter: 1–10 nm; Length 0.5–20 um; BET: 25–35 m ² /g; Electronic Resistivity: 0.75–0.1 Omu.cm (20–180 MPa); Colour: black; Bulk density: 0.06–0.08 g/cm ³ ; True density: 1.9 g/cm ³
Carbon Nanofibre	EC/116/08	Applied Sciences Inc.	Diameter 70–200 nm Length 2–5 micron
Carbon Nanofibre	EC/117/08	Applied Sciences Inc.	Diameter 70–200 nm Length 2–10 micron
Iron	EC/147/07	Nanostructured and Amorphous Materials Inc.	Iron powder (Fe) (partially passivated), Purity: 99.5% (metal basis), APS: 25 nm SSA: 40–60 m ² /g, Color: black, Morphology: spherical, Bulk density: 0.10–0.25 g/cm ³ , True density: 7.87 g/cm ³
Zinc	EC/152/07	Nanostructured and Amorphous Materials Inc.	Zinc (Zn); Purity 99.5%; APS: 130 nm; SSA: 6.4 m ² /g; Colour: Grey; Morphology: spherical; Bulk density: 0.7–0.85 g/cm ³ ; True density 7.14 g/cm ³
Copper	EC/148/07	Nanostructured and Amorphous Materials Inc.	Copper (Cu) (partially passivated), Purity: 99.8% (metal basis), APS: 25 nm SSA: 30–50 m ² /g, Color: black brown, Morphology: spherical, Bulk density: 0.15–0.35 g/cm ³ , True density: 8.94 g/cm ³

Table 2. Commissioning powders

Powder	Sample number	Supplier	Comment
Lycopodium	EC/026/08	Fluka	Sieved to 63 micron
Aluminium nanopowder	EC/060/07	Intrinsiq	Ref: PQN301 Batch 17 Estimated 73–109 nm

pressure were measured in the 2 litre sphere for each test powder over a range of dust concentrations.

IGNITION DELAY

The ignition delay is the difference between the time the control system initiates the opening of the dust injection valve and the time of the initiation of the ignition source. The ignition delay was varied within the range 60–110 ms.

IGNITION SOURCE

Chemical igniters manufactured by Sobbe GmbH were used in the test programme. Additionally, a low energy ignition source, an electric fuse head, was assessed.

The strength of the ignition source will influence the rate of propagation of flame through the dust cloud and will therefore produce different explosion characteristics of the dust in an explosion severity test. This is demonstrated by tests done using lycopodium powder (sample EC/026/08) in the 20 litre sphere (Table 3) where the rate of pressure rise and K_{ST} values were higher with correspondingly greater strength of ignition. The P_{max} was relatively flat. The 10 kJ igniter is used in the standard 20 litre sphere test (BS EN 14034-1: 2004 and BS EN 14034-2: 2006) and clearly produces the highest rate of pressure rise. A test with aluminium nanopowder (sample EC/060/07) is also shown in Table 3.

A range of tests were performed in the 2 litre sphere with lycopodium (sample EC/026/08) and aluminium (sample EC/060/07) to assess the effect of the ignition strength on the explosion characteristics in the smaller vessel (Table 4). As expected, the rate of pressure rise increased with increasing ignition strength. Table 4 shows that with an electric fuse head, the rate of pressure rise

Table 3. 20 litre sphere tests

Ignition source	P_{max} (barg)	dP/dt (bar/s)	K_{St} (bar m/s)
<i>Lycopodium (sample EC/026/08)</i>			
Electric fuse head	6.5	243	66
1 kJ Sobbe	7.3	551	150
5 kJ Sobbe	7.0	620	168
10 kJ Sobbe	7.3	673	183
<i>Aluminium (sample EC/060/07)</i>			
10 kJ	9.8	1200	326

achieved with lycopodium was only 200 bar/s, and in some cases ignition was not achieved.

At the other extreme, tests with a 5 kJ igniter tended to result in high rates of pressure rise and in the case of lycopodium was close to the 20 litre sphere results but the aluminium far exceeded the 20 litre sphere results. The P_{max} of the lycopodium was generally much greater than the 20 litre sphere tests whilst the aluminium was comparable. The 5 kJ igniter therefore had a tendency to over-drive the explosion and this indicated that a smaller ignition source would be required for the nanopowder tests. It was considered that the 1 kJ ignition source would not over-drive the explosion and would be used for the subsequent nanopowder tests.

To assess the pressure development due to the igniter, a number of different ignition strengths were tested in the 2 litre vessel without the presence of a dust cloud. Table 5 shows the pressure-time history of each of these igniters. The 1 kJ Sobbe igniter selected for the test programme produced a pressure rise of 1.05 barg and a maximum rate of pressure rise of 75 bar/s.

DP/DT, K_{St} VALUE AND P_{max}

The close proximity of the wall of the vessel to the ignition source will tend to cause flame impingement and flame

Table 4. Effect of ignition strength on test dusts – 2 litre vessel

Ignition source	P_{max} (barg)	dP/dt (bar/s)
<i>Lycopodium (sample EC/026/08)</i>		
Electric fuse head	8.2	200
1 kJ Sobbe	8.7	882
5 kJ Sobbe	9.1	1500
<i>Aluminium (sample EC/060/07)</i>		
1 kJ Sobbe	10.8	1450
2 kJ Sobbe	9.8	1950
5 kJ Sobbe	9.5	5000

Table 5. Ignition strength in the 2 litre vessel (without dust)

Ignition source	P_{max} (barg)	dP/dt (bar/s)
Electric fuse head	0.2	3.3
1 kJ Sobbe	1.05	75
2 × 1 kJ Sobbe	1.5	154
5 kJ Sobbe	4.2	250

Table 6. Comparison of 20 litre and 2 litre test apparatus

Material	20 litre sphere results			2 litre sphere results	
	Rate of pressure rise (bar/s)	K_{St} (bar m/s)	P_{max} (bar)	Rate of pressure rise (bar/s)	P_{max} (bar)
Lycopodium EC/026/08	673	183	7.3	700	7.7
Aluminium EC/060/07	1200	326	9.8	1450	10.8
Zinc stearate EC/118/08	1080	293	7.6	1400	8.2
Coal EC/120/08	558	151	7.4	600	7.3
Toner EC/122/08	714	194	7.5	725	6.3
Carbon black EC/076/07	382	104	7.8	320	6.2
Aluminium EC/104/08	2368	643	12.0	2000	11.2

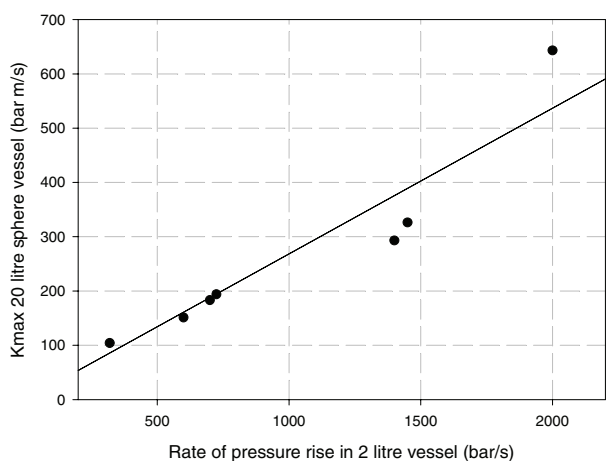


Figure 6. Commissioning results

quenching resulting in cooling effects. The rates of pressure rise were therefore lower than were needed for direct calculation of the K_{St} value using the “cubic law” equation (1).

A scaling factor was therefore established to relate the rate of pressure rise measured in the 2 litre sphere with the

K_{St} value measured in the 20 litre sphere. Table 6 and Figure 6 shows the relationship between the K_{St} /rate of pressure rise in the 2 litre vessel for a range of dusts. When a first order regression line is plotted through the data a correlation between the two vessels is obtained. The maximum explosion pressures in the two vessels were broadly comparable. To establish the K_{St} value from the rate of pressure rise in the 2 litre vessel a scaling factor of 0.268 is applied.

NANOPOWDER EXPLOSION TESTS

TEST DATA

The results obtained from the nanopowder tests in the 2 litre sphere apparatus and the MIE apparatus are presented in Table 7. Plots of the rates of pressure rise and explosion pressure against dust concentration are shown in Figures 7–13.

DISCUSSION

The nanopowders that have been tested to date have demonstrated explosion properties comparable with the micron-scale powders. For example, published data (BIA,

Table 7. Test results

Sample number	Material	P_{max} (bar g)	dP/dt (bar/s)	Equivalent K_{ST} (bar m/s)	MIE (mJ)
EC/011/09	Aluminium nanopowder (210 nm)	12.5	1677	449	<1
EC/104/07	Aluminium nanopowder (100 nm)	11.2	2000	536	<1
EC/042/08	Carbon nanofibre	5.2	62.5	17	Not measured
EC/158/07	Carbon nanofibre	6.0	112	30	Not measured
EC/116/08	Carbon nanofibre	6.9	591	158	>1000
EC/117/08	Carbon nanofibre	5.6	137	37	Not measured
EC/153/07	Multi-walled carbon nanotubes	6.4	339	91	>1000
EC/147/07	Iron	2.9	68	18	<1
EC/152/07	Zinc	5.6	377	101	3–10
EC/148/07	Copper	1.2	10	3	>1000

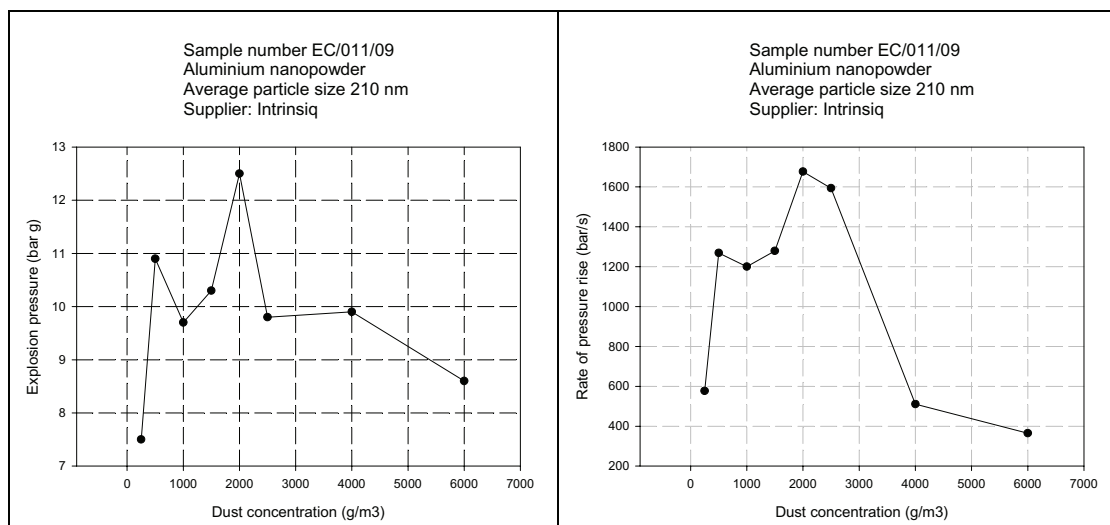


Figure 7. Aluminium sample EC/011/09 – 2 litre sphere test results

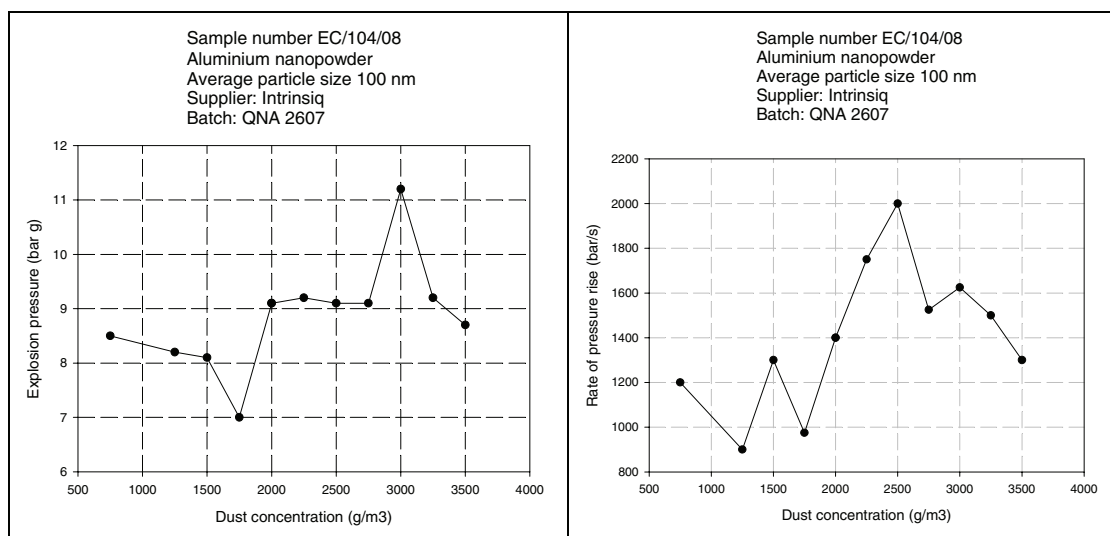


Figure 8. Aluminium sample EC/104/09 – 2 litre sphere test results

1997) shows micron-scale aluminium powders typically have K_{St} values within the range 300–700 bar m/s, and have maximum explosion pressures within the range 7–12 bar. K_{St} values of 449 bar m/s for 210 nm aluminium powder and 536 bar m/s for 100 nm nanopowder powder are well within this range of values. As might be expected, the finer aluminium sample had the higher K_{St} value. Other research workers (Nanosafe, 2008) have found the K_{St} of some aluminium nanopowders to decrease

with decreasing particle size. This has been attributed to the thin oxide layer wrapping the passivated nanoparticles; this may make them less explosible than micron-scale aluminium nanopowders. The aluminium nanopowders are firmly in the St3 Dust Group and represent very severe explosion characteristics.

The minimum ignition energies of aluminium nanopowders were comparable with micron-scale aluminium with $MIE < 1$ mJ. The aluminium nanopowders are

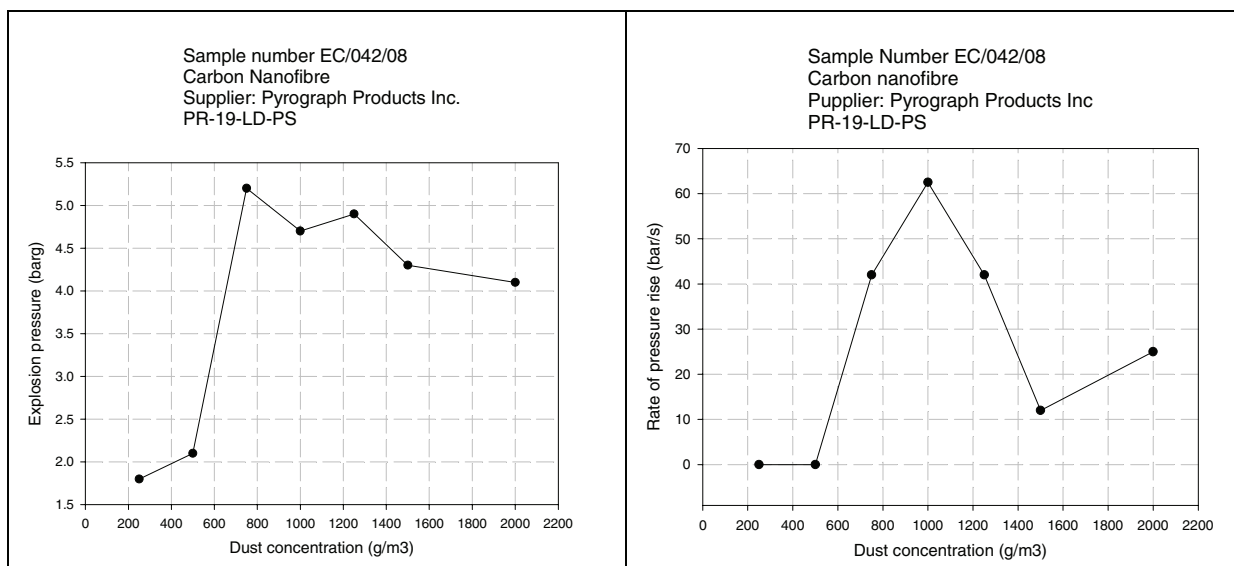


Figure 9. Carbon nanofibre sample EC/042/08 – 2 litre sphere test results

therefore very sensitive to ignition by electrostatic discharge and extreme caution is required when handling these powders.

The carbon nanopowders generally had a very agglomerated appearance and had poor handling characteristics in that they would not flow in the manner of free-flowing powders. K_{St} values were within the range 17–158 bar m/s and are therefore classified as St1 dusts and are weak to moderately explosible. The difference in the reactivity of the two extremes may be due to the

length of the fibres. The lowest rated powder Figures EC042 is a nanofibre with relatively long fibres; the diameter was 100–200 nm diameter and the fibre length was 30–100 micron long. The highest rated material was carbon nanofibre sample EC/116/08; this had a diameter of 70–200 nm but a significantly shorter length of 2–5 micron. The minimum ignition energies of these materials were greater than 1000 mJ and therefore the materials are not sensitive to ignition from electrostatic ignition sources.

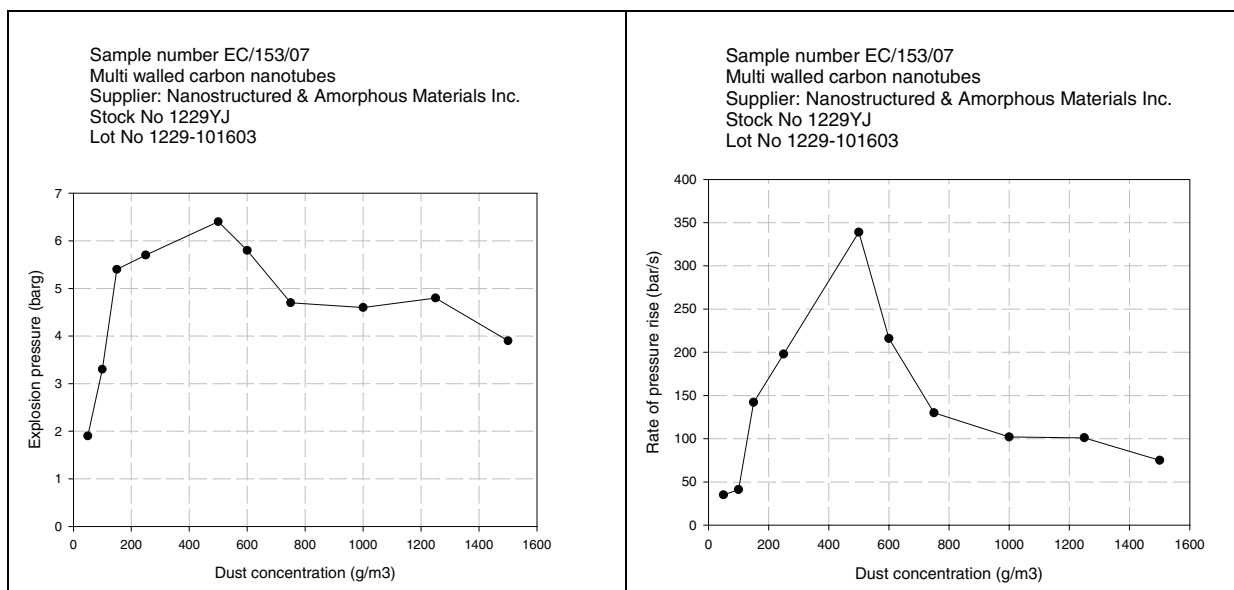


Figure 10. Carbon nanotubes sample EC/153/07 – 2 litre sphere test results

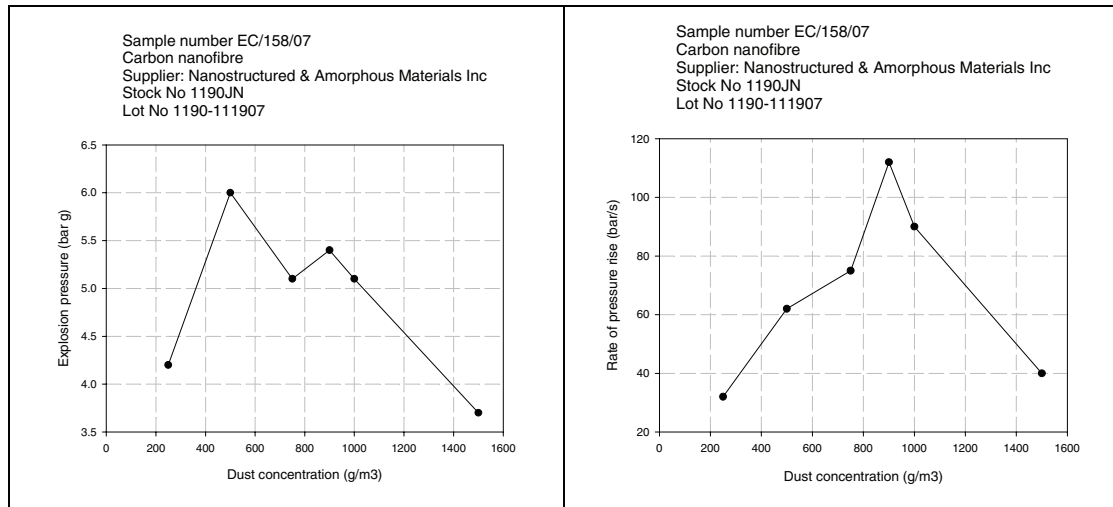


Figure 11. Carbon nanofibre sample EC/158/07 – 2 litre test results

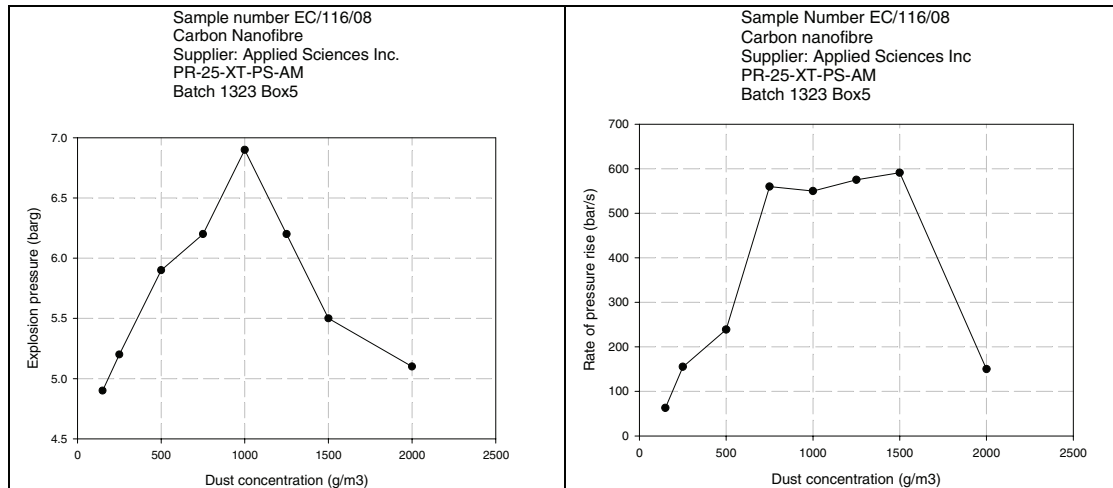


Figure 12. Carbon nanofibre sample EC/116/08 – 2 litre test results

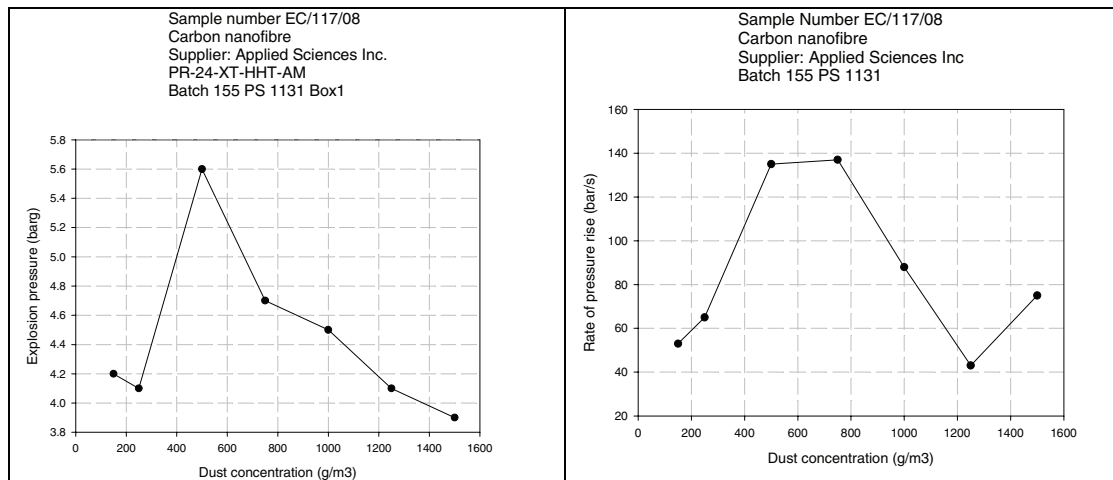


Figure 13. Carbon nanofibre sample EC/117/08 – 2 litre test results

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