Journal of Hazardous Materials 295 (2015) 97–103

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

# Potential explosion hazard of carbonaceous nanoparticles: Explosion parameters of selected materials

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## HIGHLIGHTS

- Concentration and ignition energy scans were conducted on carbon nanoparticles.
- Nanocarbons are confirmed to be in European Dust Explosion Class St-1.
- Nanocarbons exhibit MEC  $10^1$–$10^2$ g/m$^3$.
- Nanocarbons exhibit MIE  $10^2$–$10^3$ J.
- Nanocarbons exhibit $MIT_{cloud}$ > 550 °C.

## ARTICLE INFO

*Article history:*
Received 29 January 2015
Received in revised form 29 March 2015
Accepted 30 March 2015
Available online 1 April 2015

*Keywords:*
Explosion hazard
Dust
Carbon
Nanoparticle
Nanomaterials

## ABSTRACT

Following a previous explosion screening study, we have conducted concentration and ignition energy scans on several carbonaceous nanopowders: fullerene, SWCNT, carbon black, MWCNT, graphene, CNF, and graphite. We have measured minimum explosive concentration (MEC), minimum ignition energy (MIE), and minimum ignition temperature ($MIT_{cloud}$) for these materials. The nanocarbons exhibit MEC $10^1$–$10^2$ g/m$^3$, comparable to the MEC for coals and for fine particle carbon blacks and graphites. The nanocarbons are confirmed mainly to be in the St-1 explosion class, with fullerene, at $K_{St}$  200 bar-m/s, borderline St-1/St-2. We estimate MIE  $10^2$–$10^3$ J, an order of magnitude higher than the MIE for coals but an order of magnitude lower than the MIE for fine particle graphites. While the explosion severity of the nanocarbons is comparable to that of the coals, their explosion susceptibility (ease of ignition) is significantly less (i.e., the nanocarbons have higher MIEs than do the coals); by contrast, the nanocarbons exhibit similar explosion severity to the graphites but enhanced explosion susceptibility (i.e., the nanocarbons have lower MIEs than do the graphites). $MIT_{cloud}$ > 550 °C, comparable to that of the coals and carbon blacks.



## 1. Introduction

This is the second of two articles describing our work on the explosibility of nanoscale carbonaceous materials. Our first article [1] surveyed the general potential for these materials to explode. This second article reports detailed explosion parameter measurements on selected materials from that initial screening survey.

In [1], we reported on an explosion survey of a variety of carbon nanomaterials: fullerene, single-walled carbon nanotubes (SWCNTs), multi-walled carbon nanotubes (MWCNTs), carbon nanofibers (CNFs), carbon blacks, graphites, graphene, and diamond. In that survey, we attempted to explode these powders at a fixed dust concentration ($c$ = 500 g/m$^3$) with an initiating energy of 5 kJ; explosion parameters at that concentration were reported as maximum explosion pressure, $P_m(500)$, and explosion severity index, $K(500) = V^{1/3} dP/dt|_{max}(500)$. From that survey, we concluded that each of these materials has the potential to explode, and with a severity that places it tentatively in the St-1 explosion class. In this paper, we report on a more detailed examination of the explosion parameters ($P_{max}$, $K_{St}$, MEC, MIE) for a representative set of these materials.

### 1.1. Previous work

Dust explosion texts [2,3] do not discuss the explosion of powders of particles smaller than 10 μm. The IFA explosion database

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http://dx.doi.org/10.1016/j.jhazmat.2015.03.069
0304-3894/

[4] tabulates dust explosivity test data for micrometer-, but not nanometer-, sized powders. A literature review [5] of the explosion and flammability hazards of nanopowders primarily discusses micron-sized powders. The limited nanomaterial explosibility data motivated our earlier screening study [1] and the present, more detailed, investigation of explosion parameters.

There is an extensive literature on the explosion parameters for coal dust [1]. Typically, $P_{max}$  6–7 bar, and $K_{St}$  40–60 m-bar/s; the minimum explosive concentration can be as low as MEC  60 g/m$^3$; the minimum ignition energy may be as low as MIE  30 mJ; and the minimum cloud ignition temperature is in the range MIT  450–1100 °C.

Explosion studies have also been conducted on several pure carbon systems: carbon blacks [6–8] and graphite [9,10]. These are also summarized in [1]: $P_{max}$  6–8 bar, $K_{St}$  10–140 m-bar/s, MEC  40–150 g/m$^3$, MIT  650–900 °C, all comparable to the coals. The minimum ignition energy, MIE  $10^0$–$10^1$ kJ, was only measured for the fine particle graphites, and this is several orders of magnitude higher than the MIE for the coals. With the exception of the graphite MIE, the explosion parameters for finer carbon materials are generally quite similar to those of the coarser coals.

### 1.2. Recent nanopowder work

Using the standard 20-L explosion sphere [11,12], Vignes et al. [13] assessed the explosion severity ($P_{max}$, $K_{St}$) and explosion sensitivity (MIE, MEC) of various carbon black powders (Corax N115, Thermal Black N990, Corax N550, Printex XE2), one unidentified carbon nanotube (which we believe to be an Arkema MWCNT), and nano-Al. These Nanosafe2 results have been reported in several places [14–16], not always with identical values. Bouillard et al. [14,15,17] highlighted the high potential for explosion risks of only the metallic nanoparticles in manufacturing facilities. For both the carbon blacks and the Nanosafe MWCNT [13], MEC  60 g/m$^3$ (comparable to the coals) and MIE > 1 J (an order of magnitude higher than that of the coals); MIT was not determined.

In a recent review [18], explosibility data on nanomaterials is taken mainly from the Nanosafe2 project.

### 1.3. Previous results on the size-dependence of explosion parameters

#### 1.3.1. Explosion severity

As particle size decreases (and specific surface area increases), the explosion severity increases [1].

#### 1.3.2. Minimum explosive concentration (MEC)

The MEC, the lowest dust concentration at which an ignition can be achieved, typically decreases as the particle size decreases but then exhibits a plateau below a limiting particle size [3,19]; however, Pittsburgh coal may exhibit a shallow minimum in MEC as a function of particle size at $d$  30 μm [20].

For low volatility (sub-20 μm) Pocahontas coal fines, MEC  80 g/m$^3$; for high volatility (sub-20 μm) Pittsburgh coal fines, MEC  85 g/m$^3$ [20]. For polyethylene, MEC exhibits a plateau at 50 g/m$^3$ for $d$ < 80 μm [3,19], although perhaps MEC  30g/m$^3$ for $d$  10 μm [21].

For the uncharacterized Nanosafe MWCNT [13], MEC  60 g/m$^3$, comparable to that found for various coals and carbon blacks [1,15].

#### 1.3.3. Minimum ignition energy (MIE)

The MIE, the minimum spark energy required to ignite a dust cloud, strongly depends on particle size, with no obvious plateau, even at micrometer particle sizes [3]. MIE should vary with the cube of the particle diameter [22]. Experimental results for polyethylene powder are consistent with this scaling [3,23,24]; for particle sizes in the range 25–250 μm, 10 mJ < MIE < 3000 mJ (the low end of this range is only slightly higher than the MIE for gases and vapors [24]).

For metallic nanopowders, MIE < 1 mJ [23,25,26]. This low MIE puts these nanopowders at a higher ignition risk than similar micrometer-sized dusts, e.g., ignition as a result of electrostatic spark, collision or mechanical friction [18,23,25]. It is important to assess whether carbonaceous nanopowders exhibit such low MIE values.

#### 1.3.4. Minimum ignition temperature (MIT)

The MIT, the lowest temperature at which a dust cloud or a dust layer will propagate combustion, appears to decrease with decreasing particle size [8] and may be concentration dependent [27].

Using isothermal themogravimetry and thermal differential analysis, NanoSafe determined [14] onset temperatures for combustion, but not dust cloud or layer explosion temperatures.

As MIT has not been measured previously for any carbonaceous nanomaterials, our results represent the first such measurements and, as such, are an important quantification of nanocarbon explosion susceptibility.

### 1.4. Mechanisms that yield a limiting particle size

#### 1.4.1. Limiting particle size arising from reaction mechanism

A limiting particle size can be understood in the context of the various steps in the reaction mechanism [1].

#### 1.4.2. Limiting particle size arising from agglomeration

It is suggested that agglomeration reduces the explosion severity of nanosized particles [18]. Agglomeration inhibits dispersion of fine, cohesive powders into a cloud of primary particles, since the aerodynamic forces are insufficient to disrupt the inter-particle attraction [14]. Similarly, agglomerates re-form in the dust cloud as a result of collision between particles, the coagulation rate being greater for the smaller particle sizes [23]. As a result of the incomplete dispersion and subsequent coagulation, the effective particle size will be greater than the primary (nm) particle size, thereby decreasing the explosion severity [28].

While the NanoSafe multi-walled carbon nanotubes have a very high specific surface area, when compared to carbon black (Corax, Printex, and Thermal Blacks), they exhibit 200 μm agglomerates; Bouillard et al. [14] argue that this large agglomerate size reduces the explosion severity of the carbon nanotubes, compared with that of the carbon blacks.

## 2. Experimental methods

Explosion experiments were conducted at Fauske & Associates, LLC (Burr Ridge, IL).

### 2.1. Explosion severity

Descriptions of the test method [11], protocol and correction factors have been discussed in [1]. The initial screening test [1] was performed at a nominal dust concentration $c$ = 500 g/m$^3$, and the explosion parameters were reported as $P_m(500)$, $K(500)$.

The Siwek 20-L chamber, used in our studies, is described in [1]. A slightly different 20-L chamber (USBM 20-L, also known as PRL 20-L) has been utilized at the US Bureau of Mines, Pittsburgh Research Lab [29–31] in their extensive studies of explosion hazards of coal dusts.

Dust dispersion is comparable in the USBM 20-L and 1-m$^3$ chambers [32]. Enhanced aggregate break-up occurs in the dispersion of coal dusts in the Siwek 20-L [33]; of the two Siwek designs, the