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Potential explosion hazard of carbonaceous nanoparticles: screening of allotropes

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ABSTRACT

There is a concern that engineered carbon nanoparticles, when manufactured on an industrial scale, will pose an explosion hazard. Explosion testing has been performed on 20 codes of carbonaceous powders. These include several different codes of SWCNTs (single-walled carbon nanotubes), MWCNTs (multi-walled carbon nanotubes) and CNFs (carbon nanofibers), graphene, diamond, fullerene, as well as several different control carbon blacks and graphites. Explosion screening was performed in a 20 L explosion chamber (ASTM E1226 protocol), at a concentration of 500 g/m^3, using a 5 kJ ignition source. Time traces of overpressure were recorded. Samples typically exhibited overpressures of 5–7 bar, and deflagration index $K_{St} = V^{1/3}$ $(dP/dt)_{max} \sim$ 10–80 bar m/s, which places these materials in European Dust Explosion Class St-1. There is minimal variation between these different materials. The explosive characteristics of these carbonaceous powders are uncorrelated with primary particle size (BET specific surface area).

1. Introduction

Under certain conditions, engineered nanomaterials may pose a dust explosion hazard. Some nanoparticles may even spontaneously ignite when exposed to air [1] or to light [2]. Very little is known about the potential explosivity of materials when subdivided down to the nano-scale.

This is the first of two articles describing our work on carbonaceous nanomaterials. This first article reports on our survey of carbonaceous allotropes to screen for their potential explosivity. A second article [3] reports on detailed explosion parameter measurements on selected materials.

We have measured explosion parameters of several carbon nanomaterials: fullerene, single-walled carbon nanotubes (SWCNTs), multi-walled carbon nanotubes (MWCNTs), carbon nanofibers (CNFs), carbon blacks, graphites, graphene, diamond. Such measurements have not been previously made. Explosion experiments were conducted in a 20-L chamber that has been utilized extensively to characterize the explosion characteristics of coal dust. Attempt is made to correlate these explosion parameter measurements with specific surface area. Measured parameters include maximum explosion pressure, P_m, and explosion severity index, $K = dP/dt|_m \, V^{1/3}$, derived from the maximum rate of pressure rise, $dP/dt|_m$.

1.1. Introductory remarks

A dust explosion may occur as the result of dust particles being suspended in the air under confinement and exposed to an ignition source [4–6]. Most organic materials, if finely divided and dispersed in air, will explode if ignited by a sufficiently strong ignition source [5].

Industrial dust explosions have been documented since the 1785 Giacomelli flour warehouse explosion in Turin [7,5]. More recent dust explosions have resulted in significant property damage, injury and loss of life (e.g. 2008 Imperial Sugar explosion, Port Wentworth, GA [8]; 2010 Upper Big Branch Mine coal dust explosion, Montcoal, WV [9]).

Over the past decade, nanomaterials (ultra-fines) have been the subject of extensive research due to their enhanced properties, some of which derive from their large specific surface area [10]. As the production and use of nanomaterials increases (e.g. industrial production of carbon nanotubes [11–13]), associated risks will also increase. Knowledge about the physico-chemical hazards related to these new materials remains limited [14], in particular, the potential for dust explosion [15,16]. This raises the concern of the

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potential hazard of nanopowder fires and explosions [17,18]. Explosion hazards may exist for processes such as mixing, grinding, drilling, sanding, and cleaning [19–21].

1.2. Previous work

1.2.1. Overview

Dust explosion texts [4,5] do not discuss the explosion of powders of particles smaller than 10 μm. The IFA explosion database [22] lists dust explosivity test data only for micrometer-sized powders. A literature review [18] of the explosion and flammability hazards of nanopowders again primarily discusses micrometer-sized powders. Nanomaterial explosibility data thus remain limited. It is unknown whether extrapolation of explosion and flammability studies from micron-sized powders to nanopowders is valid.

Two classes of nanomaterials have elicited the most attention: carbonaceous nanoparticles and metallic nanoparticles. The nanometals exhibit more severe explosions than do the nano-carbons [1,21]. However, the chemical reaction pathway for metallic nanoparticle explosion is qualitatively different from the pathway for carbon nanoparticle explosion, and it is an oversimplification to treat both classes interchangeably. This paper focuses exclusively on the measurement of the explosion parameters for carbonaceous nanomaterials.

In 1845, Faraday and Lyell [23] suggested that coal dust could provide additional fuel for colliery explosions initiated by methane gas ignition. There is an extensive literature on coal dust explosion parameters (Supplemental Material). Particle sizing was rarely attempted in the early experiments, although the later studies [24,25] can be extrapolated to zero particle size. Typically, $P_{max} \sim$ 6–7 bar, $K_{St} \sim$ 40–60 m bar/s, MEC ∼ 60–200 g/m^3, MIE ∼ 30–200 mJ, and $\mathrm{MIT}_{cloud} \sim$ 450–1100 °C.

Explosion studies have also been conducted on several pure carbon systems: carbon blacks [26–28] and graphite [29,30]. For most of these materials, $P_{max} \sim$ 6–8 bar, $K_{St} \sim$ 10–140 m bar/s, MEC ∼ 40–150 g/m^3, MIT ∼ 650–900 °C, comparable to the coals; a nonrigorous lower bound of MIE ∼ 1 mJ would be considerably lower than that of the coals.

1.2.2. Recent nanopowder work

Using the standard 20 L explosion sphere [31], Vignes et al. [14] 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), and one unidentified carbon nanotube (which we believe to be an Arkema MWCNT). These Nanosafe2 results have been reported in several places [32,33], not always with identical values. Bouillard et al. [32,34,35] observed that carbon nanopowders exhibit a low propensity to explode while metallic nanopowders can be very reactive; they, therefore, highlighted the high potential for explosion risks of only the metallic nanoparticles in manufacturing facilities. The explosion parameters for the carbon materials from the NanoSafe 2 studies are included in Table 1, where, for several of the entries, we have chosen the most likely of the reported values.

Work has also been done, using a (non-standard) smaller 2 L chamber, on several allotropes of carbon: MWCNT, CNF and carbon black [36]. The explosion parameters, as measured in this smaller chamber, are suspect, since the proximity of the quenching external surface acts as a heat sink and will tend to suppress any developing explosion (Section 4.4). Vignes et al. [14] and Dufaud et al. [16] have questioned the applicability of even the larger 20 L sphere data to assess the risk from nanopowders. Hence, the explosion parameters from the 2 L chamber studies have not been included in Table 1.

Worsfold et al. [21] review uncritically the results on the explosibility of nanomaterials, with data taken mainly from the Nanosafe2 project.

1.2.3. Previous results on the size-dependence of explosion parameters

1.2.3.1. Explosion severity. In general, as particle size decreases (and the specific surface area increases), the explosion severity, as indicated by P_{max}, and $(dP/dt)_{max}$, increases. However, for the few materials studied, as the particle size is reduced below ∼ 50 μm, severity ceases to increase. This quasi-plateau has been attributed variously to particle agglomeration and/or reaction mechanisms.

For coal, as the particle size is decreased, there is no further increase in either P_{max} or $(dP/dt)_{max}$ below ∼ 50 μm [5]. Similarly, P_{max} exhibits a plateau at particle sizes < 50 μm for flour and < 40 μm for methylcellulose [37,38]. For polyethylene, P_{max} exhibits a plateau for particle sizes < 50 μm [37,38]. Polyvinyl chloride (PVC) behaves differently: P_{max} continues to increase in the particle size range 25–150 μm. Explosion severities (P_{max}, K_{St}) for the uncharacterized NanoSafe CNTs are comparable to those found for coals and nanostructured carbon blacks.

1.2.3.2. Other explosion parameters. Discussion of minimum explosive concentration (MEC), minimum ignition energy (MIE) and minimum ignition temperature (MIT) is discussed in [3].

1.2.4. Possible origin of a limiting particle size

1.2.4.1. 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 [39]. In the case of a coal dust explosion (or any other organic material), combustion primarily occurs in the homogeneous gas phase. The combustion rate of the dust cloud depends on the relative time constants of the three processes: devolatilization, gas phase mixing and combustion. Particle size primarily influences the devolatilization rate; a higher specific area allows more rapid devolatilization. However, if gas phase combustion is the rate limiting step, increasing the devolatilization rate (by decreasing the particle size) will not increase the overall combustion rate.

For the case of coal, the maximum explosive severity is achieved for particle size ∼50 μm; smaller, micron-sized coal particles do not further increase the severity. The particles must undergo heating, melting, devolatilization, and the combustion reaction occurs in the gas phase. For sub-micron coal particles, the heating, melting and vaporization processes occur more quickly than the gas phase reaction process, which latter becomes the rate determining step. The severity of a nano-coal dust explosion is not expected to increase because the rate limiting step is the vapor combustion [18,15].

Intrinsically stable carbon allotropes may have more inhibited devolatilization; thus a smaller particle size might be needed for the devolatilization rate to compete with the combustion reaction rate.

1.2.4.2. Limiting particle size arising from agglomeration. The possibility [21] that agglomeration reduces the explosion severity of nanosized particles is discounted in [3].

2. Experimental methods

Explosion experiments were conducted at Fauske & Associates, LLC (Burr Ridge, IL). BET specific surface areas were measured at Pacific Surface Science (Ventura, CA). Transmission electron microscopy (TEM) was performed at the NIOSH Alice Hamilton Lab (Cincinnati, OH).