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Nanotecholog-E: Explosivity

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Introduction

Nanotechnology—the engineering and processing of near atomic scale materials and structures, 100 nanometers or less, has been billed as the new Industrial Revolution. Nanotechnology applications promise miraculous advancements in fields such as medicine, electronics, cosmetics, coatings, packaging, and energy. Over the next few years, nanotechnology's global economic impact is expected to exceed one trillion dollars. Nanotechnology's luminance brings with it new challenges to the assessment of its potential impact on environmental safety and health. These tiny materials with large reactive surface areas exhibit unique new properties and applications that are just beginning to be assessed from a health and safety standpoint. While some excellent guidance has been developed by the U. S. National Institute of Occupational Safety and Health in their Approaches to Safe Nanotechnology publication, guidance on fire protection remains scarce.[1] Engineered nanomaterials are expensive to produce and beyond potential safety and environmental concerns, combustibility issues also impact company operational expenses and business continuity.

Nanomaterial Explosivity: Similarities and Unknowns

Nano-sized particles and powders are commonly referred to as nanomaterials. Nanopowders are composed of particles in this size range from about 1 – 100 nanometers (nm). One nanometer is equivalent to 10^{-9} meter. This is particularly noted in comparison to the definition of a combustible *dust*, which indicates a particle size of 500 microns (μ) or smaller (35 mesh). The intent of this section is also to provide a brief overview of the existing literature to clarify the commonalities and differences of micron-sized dust vs. nanoparticulate as they relate to traditional fire protection hazards and to highlight the fundamental basis of the available and sometimes contradictory data to assist the safety professional.

Some examples of nanopowders include metals; metal oxides, borides, carbides, nitrites and sulfides, and nonmetal materials such as various forms of carbon, clay silica and silicon carbides.

[1] National Institute for Occupational Safety and Health, "Approaches to Safe Nanotechnology," March, 2009.

Nanopowders are produced in several forms including spheres, flakes (e.g., aluminum), fibers (e.g., Teflon and other polymers) and tubes (e.g., carbon nanotubes).

The explosion hazards of nanopowders have not been widely addressed within existing research literature or documented within the fire protection community. To minimize the risk of dust explosion involving nanomaterials, the potential hazards of the specific material must be appropriately understood. At issue is the lack of overall data in the fire protection and research community addressing specific explosibility potential for various nanopowders. There is, however, significant documentation detailing the explosion characteristics of micron-sized powders (particles with size range of 10 - 500 µ).

It should be noted that as part of NIOSH Strategic Plan for Nanotechnology Research, there is clear recognition of the need for additional test data, specifically "to identify physical and chemical properties that contribute to dustiness, combustibility, flammability, and conductivity of nanomaterials. To investigate and recommend appropriate work practices to eliminate or reduce the risk to explosions and fires."[2] As federal funding was recently made available to expand knowledge in this area, NIOSH will begin some early new explosibility experiments on nanomaterials within the U. S. beginning in the Spring of 2010.

Key Definitions and Terms

Below is an overview of several key terms and concepts important for understanding the explosion potential of dusts:

K_{st}: One of the most important terms when dealing with explosibility measurements and dust explosibilty is constant K_{st}, which is defined as the maximum rate of pressure rise of a dust explosion in a 1 m³ vessel. The test method used to obtain this constant is standardized worldwide. The value of the K_{st} is used to characterize the reactivity and explosive ability of a particular dust.[3]

1-50	Very weak and explosibility
50-100	Weak
100-200	Moderate
200-300	Strong
300+	Very Strong

Safety engineers may also hear reference to the following dust explosion hazards:

St 0 dust (K_{st} = 0)
St 1 dust (K_{st} >0-200)
St 2 dust (K_{st} 201-300)
St 3 dust (K_{st} >300)

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[2] U. S. National Institute of Occupational Safety and Health, "Strategic Plan for NIOSH Nanotechnology Research: Filling the Knowledge Gaps", March 2008.

[3] National Fire Protection Association, Standard 654 for the Prevention of Fire and Dust Explosions.

Minimum Ignition Energy or MIE is the minimum amount of thermal heat energy released at a point in a combustible mixture to cause indefinite flame propagation under specified test conditions. To simplify this concept, a combustible dust with a low MIE <10 milliJoules (mJ) subsequently requires a very weak ignition source, or very little energy such as a static discharge, to ignite it.

Minimum Explosible Concentration (MEC, C_{min} measured in g/m^3) is the lowest concentration of a dust that can support a self-propagating explosion. Essentially MEC is the same thing as lower explosion limit (LEL) or lower flammable limit (LFL), but these terms are not typically used when discussing dust explosions. Generally, the MEC tends to decrease with decreasing particle size. Thus the MEC and LEL are lower for smaller particle dust.[4]

Nanopowder Research – A Brief Literature Review

Explosive dust clouds can be generated from most organic materials, many metals, and some non-metallic inorganic materials. Dust explosions involving particle sizes ranging from a few microns (one micron is equivalent to 10^{-6} meter) to hundreds of microns have been extensively studied within the research community.

Nanoparticles of combustible materials present the potential for a dust explosion hazard. However, the explosion potential for nanomaterials is not adequately understood due to an overall lack of empirical data within the scientific & fire protection community. Additionally, the small body of available data is sometimes based on older experimental testing apparatus and techniques which may not have been suitable for testing nano-sized particles, which may result in inaccurate findings and conclusions.

Most materials, including all organic materials, will burn if enough heat is applied to them. The safety engineer must consider the variables of the explosion pentagon when determining potential for combustible dust explosion hazards:

1. Fuel
2. Oxidizer
3. Ignition Source
4. Suspension
5. Confinement

The NFPA Fire Protection Handbook elaborates on the explosion pentagon by stating “the chances of a dust cloud igniting is governed by the size of its particles, dust concentration, impurities present, oxygen concentration, and the strength of the source of ignition.”[5] The handbook continues by stating “Dust clouds can be ignited by open flames, lights, smoking materials, electric arcs, hot filaments of light bulbs, friction sparks, high pressure steam pipes and other hot surfaces, spontaneous heating, welding and cutting torches and sparks from these operations, and other common sources of heat for ignition.”[6]

It is generally accepted that as particle size decreases for a combustible dust, or powder, that the amount of energy needed to ignite a material also decreases. The temperature onset of

[4] Ibid.
[5] National Fire Protection Association, NFPA Fire Protection Handbook Vol I, 12 ed. p 6-141).
[6] Ibid.

combustion generally tends to decrease as particle size decreases and surface area increases. In addition, the finer the particle the more intensely it burns. This results in faster fire spread or a greater potential for there to be an explosion under the right conditions.

The theory appears to hold true for certain specific nanomaterials, such as carbon nanotubes (CNTs). For example, recent CNT testing indicated that "studied carbon nanotubes exhibit explosion severities and sensitivities of the same order as those found for various coals, food, flours, and other nanostructured carbon blacks."[7]

The report also indicates that the "onset temperature of carbon materials strongly depends on the specific surface area of those materials" and that "the decrease of temperature onset with the increase of the specific surface area can be explained not only by the increase of the specific surface, but also by the decrease of the activation energy of the combustion reaction between carbon and oxygen."[8]

The recent CNT findings are consistent with the traditional fire protection theory available to the fire protection community as detailed earlier. "The finer the particle size, decreased moisture content, increased turbulence, greater oxygen concentration and the presence of a flammable vapor or gas all increase the burning velocity, and surface properties such as surface roughness also have an effect. For a given weight concentration of dust, a coarse dust will show a lower rate of pressure rise than a fine dust." [9]

There are always exceptions to the rules. A 2004 UK Health and Safety Laboratory (HSL) Literature Review conducted by DK Pritchard details the generally accepted principle of increased ignitability and explosion violence as a function of particle size. As the particle size of a combustible dust becomes smaller, based on existing scientific data for combustible dust in the micron scale, the explosion severity generally increases: "the primary factor influencing the ignition sensitivity and explosion of violence of a dust cloud is the particle size or specific surface area (i.e. the total surface area per unit volume or unit mass of the dusts). As the particle size decreases the specific surface area will increase. A rough rule of thumb is that explosive clouds cannot be generated from dusts composed of particles greater than about 500 µm. The general trend is for the violence of the dust explosion and the ease of the ignition to increase as the particle size decreases, *though for many dusts the trend begins to plateau as particle sizes of the order of tens of microns. No lower particle size limit has been established below which dust explosions cannot occur*." [10] We will review recent testing results for metallic aluminum and powders which exhibit opposite effects to the generally accepted theories detailed above.

Additional Considerations

The 2004 DK Pritchard HSL literature review details a myriad of additional variables (reaction mechanisms, devolatization, oxygen concentration, etc.) beyond the traditional explosion pentagon model, which may directly impact the likelihood of dust explosion events for the micron scale powders, and possible reasons as to why some particular dusts may exhibit

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[7] Nanosafe, 2008, p. 5, http://www.nanosafe.org/scripts/home/publigen/content/templates/show.asp?L=EN&P=55&vTicker=alleza.

[8] Ibid.

[9] NFPA *Fire Protection Handbook.*

[10] Pritchard, DK. Literature Review – Explosion Hazards Associated with Nanopowders. HSL/2004/12. Harpur Hill, Buxton, SK17 9JN, March 2004.

explosion severity "limiting factors" italicized above, which are contradictory to the generally accepted trend for increased explosion severity and decreased ignition energy as a function of decreased particle size.[11]

Keeping in mind that the *general trend* is for the explosion severity to increase and the LEL / C_{min} (measured in g/m^3) and ignition energy (MIE measured in milliJoules - mJ) to decrease as particle size decreases, the following additional variables must also be considered in determining if the dust cloud can be ignited and the violence of the resulting explosion:

1. **Dust Concentration**: in terms of LEL / MEC. Values depend on dust composition, and particle size distribution. Typical values are 50-100 g/m^3 for the lower limit and 2-3 kg/m^3 for the upper limit. "Variations in minimum explosive concentration will occur with changes in particle diameter; that is, the C_{min} is lowered as the diameter of particles decreases."[12]
2. **Dust Composition**: refers to the purity and uniformity of the sample being tested, as it relates to potential reactivity with the surrounding atmosphere.
3. **Ignition Strength**: (MIE) values for dusts are typically in the range of 1 to 10 mJ.
4. **Agglomeration:** the degree of dust dispersion, greatly influenced by moisture content.
5. **Oxygen Content and Turbulence**: decreased oxygen reduces the explosion severity; it limits the rate of combustion, decreases maximum explosion pressures, and increases the ignition energy required.
6. **Moisture Content**: Moisture in dust raises the ignition temperature because of the heat absorbed during heating and vaporization of the moisture. The moisture content of a dust will affect the ease of ignition and ability to sustain an explosion. Increasing moisture content increases the ignition energy and reduces explosion violence.
7. **Solvent Content**: Flammable solvents on the dust can lower ignition energy and increase explosion violence.
8. **Electrostatic Charges**: These can build up on nanopowders during handling and processing. Nanopowders can become highly charged during usage and handling and serve as their own ignition source.

Agglomeration is a potentially critical factor worth of further discussion when understanding the explosibility of nanopowders since many nanopowders tend to agglomerate or aggregate. These powders can be wispy in nature. Very fine particles can combine or agglomerate into larger particles. Agglomeration of fine powders can result in explosion characteristics that are similar to dusts with particles of the same size as the agglomerated particles. "Nanopowders which tend to agglomerate show explosion violence characteristics of the same order as those observed with micropowders of the same substance."[13]

Failure to prevent agglomeration while testing the powder via traditional testing apparatus and techniques could result in underestimating the true explosion hazard of the material. The research community has recently been particularly careful to consider the influence of agglomeration on testing results and true explosion potential.

An additional critical variable that must be considered for nanopowders is the total *quantity* of powder being handled. Many nanopowders are produced or used only in small (gram) quantities which limit the potential for large scale explosion hazards.

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[11] Ibid.
[12] National Fire Protection Association (NFPA) *Fire Protection Handbook,* Vol I, 12 ed. p 6-142.
[13] Nanosafe, p. 4.

Debating the Accuracy of Extrapolation of Available Data from the Micron-scale to the Nano-scale

In contrast to the HSL Pritchard review, a recent Journal of Physics publication by R. Dobashi contends that one can theoretically deduce or estimate explosion potential of nanopowders based on existing micron scale data for the same material; he concludes, "the explosion risk will increase as the particle size is decreasing. This trend will continue to nanoscale, however, the *value of the explosion hazard parameter will be in the range between the value for the particle of the micro scale and that of gas*."[14]

Dobashi bases this theory on the fact that the particle size is becoming smaller and smaller in the use of nanopowders, and that the limit of the smallest particle should be at the molecular level. "*Considering that the particle size is becoming smaller and smaller, the limit of the smallest particle should be molecule. Then, comparisons between dust and gas are made on explosion hazard parameters*"[15]

Dobashi indicates that the "*explosion hazard parameters of the nanoparticles are estimated by extrapolating the trend of size dependence in micro scale to the nano scale. However, these results are just estimation*." He is responsible to report that "accumulation of measured data of the hazard parameters of the nanoparticles and detailed analysis are needed." [16]

DK Pritchard indicates, in contrast, that: "an important consideration in extrapolating the explosion characteristics for nanopowders from measurements obtained with micron scale powders is the *change in chemical properties that materials exhibit when the particle size falls below about 100 nm. Below these sizes the behavior of the particle surface starts to determine the behavior of the material. Materials that do not give explosive dust clouds when dispersed as micron scale particles may become explosive when dispersed as nanoparticles and vice versa*." He contends that "*without supporting experimental data it would be unwise to assume that a nano powder is explosive all or not based on the behavior of the powder at the micron scale*." [17]

Nanomaterials are also typically manufactured with a more uniform size range. The expectation would be that nanopowders are more easily ignited then a coarse powder of the same material. "*It has to be concluded that existing explosion data for micron scale powders cannot be extrapolated with any degree of confidence to nanopowders.* In order to assess the explosion hazard of nanopowders what is required is experimental data for a representative range of materials, at both scales, including materials that are nonexplosive at the micron scale."

The unreliability of this extrapolation or comparison is exemplified by recent NanoSafe2 test data: "Lesson: For metallic aluminum nanopowders, the small oxide layer wrapping passivated nanoparticles may make them less explosible than micropowders."[18] The findings also provide a "Warning: For aluminum, combustion mechanisms of nanosized particles are different from those observed with microsized particles. This may lead to potential problems of large scale

[14] Dobashi, R. Risk of dust explosions of combustible materials. Nanosafe 2008: International Conference on Safe production and use of nanomaterials: IOP Publishing Journal of Physics: Conference Series 170 (2009) 012029.
[15] Ibid., p. 4.
[16] Ibid., p. 5.
[17] Pritchard, p.13.
[18] Nanosafe, p. 4.

industrial storage of such particles. Advice: specific prevention and protection measures should then be taken." [19]

NFPA details additional reasons why this comparison is considered an unreliable one: "*Another reason the comparison is unreliable between Cmin (g/m^3) and the LEL of flammable gases is that explosion data for flammable gases were gathered under comparatively quiescent conditions and not turbulent ones*."[20]

Recent Data and Findings

The Nanosafe2 Project Consortium (www.nanosafe.org) has very recently provided some useful data on some of the most widely used nanopowders. The consortium includes 25 partners from 7 different countries of the EU, mainly small, medium and large enterprises and public research laboratories. The project is supported through the Sixth Framework Program for Research and Technological Development. The project started in April 2005 and ended in March 2009.

The main objective of the Consortium was to develop risk assessment and management for secure industrial production of nanoparticles. "It focuses on four areas: Detection and characterization techniques, Health hazard assessment, Development of secure industrial production systems and safe applications, and Societal and environmental aspects."[21]

The research was conducted using updated experimental apparatus and techniques, most notably a new Hartmann tube made of closed stainless steel equipped with pressure sensors, to better prevent contamination and to obtain more accurate test data. "New confined stainless steel Hartmann tube and falling hammer equipment help bring experiments to a higher degree of safety and efficiency."[22]

Experiments were performed on various carbon black powders, aluminum nanoparticles of different sizes and carbon nanotubes (CNT) in accordance with ASTM and NFPA methods and standards. The CNT results, in terms of explosion severity and sensitivity, are on the same order for various coals, food flours, and other nanostructured carbon blacks.[23] In contrast, the Kst values decreased for the aluminum powders as the size decreased, which is contradictory to generally accepted fire protection theory.[24]

There is a generally accepted inverse relationship between ignition temperature and particle size / surface area, as recorded in recent testing of carbon black by the Consortium. The onset temperature of carbon materials is strongly dependent upon the particle size and surface area of the material.

Explosivity Conclusion

Are nanopowders more or less explosive than micron scale powders of like materials? The answer is, in short, it depends. We have seen how some materials appear to conform with

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[19] Nanosafe, p. 6.
[20] NFPA *Fire Protection Handbook,* Vol I, 12 ed. p 6-144
[21] Nanosafe, p. 7.
[22] Nanosafe, p. 3.
[23] Nanosafe, p. 4.
[24] Nanosafe, p. 4.

traditional fire protection theory, while some do not. Only more data will allow the safety professional to make a more accurate estimation of explosion severity.

While nanopowders may be used in small quantities, may tend to agglomerate, or may behave uniquely based on the above detailed variables within any particular industrial process, there remains a clear need for additional testing using standard apparatus and techniques within the scientific community. Traditional fire protection theory cannot be supported, and hence explosion potential should not be estimated or extrapolated between the micron and nano scales without a strong base of empirical test data taken across a wide range of nano sized materials. We have seen how some materials, such as CNTs, tend to behave consistently and similarly with like materials at the micron scale, while others such as aluminum powder do not.

Comparison with data for micron scale powders of the same material is simply *not* a reliable estimation of the explosivity of the material in the nano particle size range and should not be considered reliable when attempting to assess the safety parameters and explosion risks of an industrial process utilizing a nanopowder. This is especially so when used in larger quantities, where the powder is uniform in nature allowing for more specific surface area, or especially where the material is organic. The degree of agglomeration and aggregation presents additional consideration factors. The only way to best determine the explosion severity is to have the specific material tested by a qualified dust expert using appropriate lab testing techniques.

The Safety Engineer is challenged to proceed cautiously when attempting to evaluate the safety of any industrial process where a deflagration potential is thought to exist. Utilization of independent testing data of the specific material based on traditional testing equipment and techniques may not provide an accurate estimation of explosion potential. Until such a body of knowledge is published and well documented, the safety professional should reach out to highly qualified dust experts to help determine the likelihood of explosion based on the many variables discussed above. The Safety Engineer is nonetheless challenged to keep abreast of new data from the scientific / research community as it is made available.

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