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**Literature review – explosion hazards associated
with nanopowders**

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EXECUTIVE SUMMARY

Objectives

Nanopowders are composed of particles in size range from about 1 to 100 nanometres (nm). One nanometre is equivalent to 10^{-9} m. The growing demand for nanopowders arises from the change in physical, chemical and electrical properties exhibited by particles when their size falls below about 100 nm. The laws of quantum physics, rather than the laws of classical physics, come into play at these small particle sizes and the behaviour of the surfaces start to dominate the bulk behaviour of the material. For example, materials that would normally be conductors of electricity can become insulators at the nanoscale, or vice versa. Titanium dioxide and zinc oxide, which are widely used in sunscreens, become transparent at the nanoscale, a cosmetically desirable property for sunscreen products. Nanopowders are also referred to as nanomaterials, nanoparticles or ultra fine particles.

Along with the increasing production and use of nanoscale particles there has been a growing concern over the impact of this new technology on health and safety and the environment. This has almost exclusively concentrated on the potential health hazards of nanopowders. One potential hazard that appears to have received little attention to date is their explosibility. A literature review has been commissioned by the Corporate Science and Knowledge Unit (CSKU) of HSE to explore the use of nanopowders in industry and the potential explosion hazards. This report presents the findings of the review and assessment of the explosion risks associated with the processing and use of nanopowders.

Main Findings

1. An increasing range of materials that are capable of producing explosive dust clouds are being produced as nanopowders. At the same time new uses of nanopowders are further adding to the demand for these powders. While some of these nanopowders are only being produced in very small quantities at present, and may continue to be for the foreseeable future, the production of others is likely to increase significantly over the next few years.
2. There is a growing concern over the impact the increased use of nanopowders and other nanomaterials will have on health and safety and the environment. These concerns are almost exclusively centred on the potential toxic effects of nanomaterials. The potential explosion hazards of nanopowders have not been addressed.
3. There is a considerable body of knowledge on the explosion characteristics of micron-scale powders (particle sizes ranging from about 10 to 500 μm). A literature search has found no data for nanopowders (particle sizes of 1 to 100 nm). It is considered that the extrapolation of the data for larger particles to the nano-size range cannot be carried out with any degree of confidence, due to marked change in the chemical and physical properties of particles below sizes of about 100 nm.

Recommendations

1. It is recommended that the explosion characteristics of a representative range of nanopowders be determined using the standard apparatus and procedures already employed for assessing dust explosion hazards. Comparison with data for micron-scale powders of the same materials will allow knowledge of particle size effects to be extended into the nanosize range.

2. Although it is recommended using standard apparatus and procedures for measuring the explosion characteristics of nanopowders, if agglomeration is thought to be occurring in the test vessel it may be necessary to modify the way the powder is dispersed. This is to ensure that the worst case characteristics will be measured.

1 INTRODUCTION

Nanopowders are composed of particles in size range from about 1 to 100 nanometres (nm). One nanometre is equivalent to 10^{-9} m. The growing demand for nanopowders arises from the change in physical, chemical and electrical properties exhibited by particles when their size falls below about 100 nm. The laws of quantum physics, rather than the laws of classical physics, come into play at these small particle sizes and the behaviour of the surfaces start to dominate the bulk behaviour of the material. For example materials that would normally be conductors of electricity can become insulators at the nanoscale, or vice versa. Titanium dioxide and zinc oxide, which are widely used in sunscreens, become transparent at the nanoscale, a cosmetically desirable property for sunscreen products. Nanopowders are also referred to as nanomaterials, nanoparticles or ultra fine particles.

Nanoparticles occur naturally, for example minute particles of salt become airborne through the action of the waves of the sea, or are an unintended but largely unavoidable by-product of combustion and other high-temperature industrial processes. Man has been using nanopowders, in the form of nano-sized pigment and carbon colourants since the beginning of recorded history. It is only, however, since the early twentieth century that nanopowders have been manufactured in bulk, for example carbon black (produced by the burning of natural gas) for use as a reinforcing agent in vehicle tyres. The real growth in the production of nanopowders, though, did not start until the mid-1970's. The current use of nanopowders is extremely broad and there are few commercial products that do not include nanoparticles. Quantities of nanopowders produced can range from large quantities (tons) of products like fumed silica and carbon black to extremely small quantities of the more precious products, for example stabilised metallic quantum dots and atomic clusters. According to an ETC Group Publication¹ at least 44 elements in the periodic Table are commercially available in nanoscale form and more than 140 companies worldwide are engaged in nanoparticle manufacture. By 2005, it is estimated that the global market for nanoparticles will come close to \$1 billion.

Along with the increasing production and use of nanoscale particles there has been a growing concern over the impact of this new technology on health and safety and the environment^{1,2}. In June 2003 the UK Government commissioned the Royal Society and the Royal Academy of Engineering to carry out an independent study of the likely developments in nanotechnology and to examine whether nanotechnology raises or is likely to raise new health and safety, environmental, social or ethical issues which are not covered by current regulation. As part of the study a workshop was held on 30 September 2003 and a report on the workshop³ is now out for public comment.

One of the main concerns over the use of nanopowders is their potential toxic effect. Particles < 70 nm can enter the lungs and deposit on the alveolar surfaces and particles < 50 nm can even penetrate cell walls. A potential hazard of nanopowders that appears to have received little attention to date is their explosibility. Most organic materials, many metals and even some non-metallic inorganic materials if finely divided and dispersed in air will explode if ignited by a strong enough ignition source. The upper size limit for the formation of an explosive dust cloud is the order of 500 μ m. The general trend is for the violence of the dust explosion and the ease of ignition to increase as the particle size decreases, though for many dusts the trend begins to plateau at particle sizes of the order of tens of microns (μ m). No lower particle size limit has been established below which dust explosions cannot occur. Ignition energies for dust clouds are usually higher than for gases or vapours, typically of the order of a fraction of a millijoule for gases and 1 to 10 millijoules for dusts. The overpressures generated by a gas or dust

explosion are, however, of comparable magnitude. There is, therefore, the potential for nanopowders to give rise to a significant explosion hazard.

A literature review has been commissioned by the Corporate Science and Knowledge Unit (CSKU) of HSE to explore the use of nanopowders in industry and the potential explosion hazards. This report presents the findings of the review and assessment of the explosion risks associated with the processing and use of nanopowders.

2 APPLICATION AND MANUFACTURE OF NANOPOWDERS

2.1 APPLICATIONS

Nanopowders are already used in a wide range of industries and developments in the use of nanomaterials are being reported almost on a daily basis in the scientific literature.

Current applications include:

- **Sunscreens and cosmetics.** Titanium and zinc oxide nanopowders are widely used in sunscreens and other creams and lotions.
- **Textiles.** Teflon and other polymer nanoscale fibres are used in some stain and wrinkle-resistant clothing.
- **Coatings.** Custom-made nanocomposites and titanium dioxide nanopowders are used in anti-scratch coatings for lenses and to treat glass surfaces to give them self-cleaning properties. New anti-graffiti coatings for walls contain nanoparticles.
- **Sports goods.** Carbon nanotubes and nanoclay particles are used in the manufacture of tennis racquets and tennis balls. Ski waxes based on nanocomposites are also available.
- **Explosives, propellants and pyrotechnics.** Aluminium nanopowders are being used instead of micron-scale powders to further enhance the burning characteristics of these materials.
- **Catalysts.** Their performance is being enhanced by using catalysts composed of nanosized materials – the greater the surface area the more effective a catalyst will be.
- **Electronic storage media.** Hard-disks based on nanostructured magnetic multi-layers currently dominate the market.
- **Filtration.** Filters made of nanofibres, for example alumina fibres, are used to trap materials such as viruses, bacteria, animal cells, endotoxins and macromolecules such as DNA. They are also used for removing trace toxic metals from water.
- **Disinfectants.** Nanoemulsions and nanoparticles of a lanthanum-based compound are being used in surface disinfectants and to prevent the growth of algae in pools and aquariums.
- **Medical uses.** Silver nanoparticles are used as an antibacterial agent for bandages and in the coatings on hearing aids.
- **Alloys and metals.** Alloys and metals are being produced with nano-crystalline structures to increase their strength. For example nanocrystalline nickel is as strong as hardened steel and nanocrystalline aluminium alloys can be up to twice as strong as their conventional equivalents.
- **Non-metallic components.** Carbon nanotubes are being used to increase the strength of automobile plastic components. Nanoparticles of diamond are being added as

reinforcing agents to rubbers, plastics and resins.

- **Abrasives.** Abrasive pastes made from diamond nanopowders are being used for high precision polishing of lenses and mirrors in optical instruments.
- **Lubricants.** The lubricating properties of oils are being improved by the addition of diamond nanopowders.

Applications currently under development, some of which are likely to be commercially available in the next year or so, include:

- **Batteries.** Prototype batteries using nanoparticles have been developed that offer ten times the charge rate of conventional rechargeable batteries.
- **Solar cells.** Cells based on tiny structures called nanorods, that can be tuned to respond to different wavelengths, are currently under development. Another type of cell under development is one that produces hydrogen rather than electricity.
- **Fuel cells.** Nanostructured catalysts look as if they may be a critical component in finally making fuel cells a reality. The other impact nanotechnology will have is on the way fuel is stored in the fuel cells. The nanotube shows promise as a storage medium for hydrogen and there are plans to shortly launch a methane-based fuel cell for powering mobile phones and laptops, which will use nanohorns, a relative of nanotubes, for the fuel storage.
- **Light sources.** A light bulb, driven by nanotubes, which promises to match or exceed the efficiencies achieved with fluorescent lighting is under development.
- **Electronic storage media.** A number of nanotechnologies are promising new types of RAM for computers that would be non-volatile (ie the information stored in the RAM would not be lost when the power is turned off) and could have enough capacity to make disc storage unnecessary for applications such as personal computers. One example of this type is magnetic RAM (MRAM), which has already seen some limited commercial use.
- **Display technologies.** Flat-panel electronic displays, for example a hang on the wall television screen, based on nanotubes, will soon be commercially available.
- **Bioanalysis and biodetectors.** Nanoparticles small enough to behave as quantum dots can be made to emit light at varying frequencies. Efforts to exploit this property for bioanalysis are being pursued by a number of companies. For example, by getting particles that emit at different frequencies to attach to different molecules it would then be possible to spectroscopically determine the presence of many substances in one sample. Others are exploiting the sensitivity of the electrical properties of nanowires and nanotubes to develop highly sensitive biodetectors that could reveal the presence of a single molecule. Nanostructured materials, coupled with liquid crystals and chemical receptors offer the possibility of cheap, portable biodetectors that might, for instance, be worn as a badge.
- **Drug delivery.** Drug delivery is an area that is already showing significant impact from nanotechnology, with some approaches using nanoparticles or nanocapsules to deliver drugs through the skin, lungs, stomach and eyes already in clinical trials and

many more in pre-clinical trials. The potential advantages of these approaches are many and include increased solubility and resistance to gastric enzymes (offering oral delivery of drugs that previously needed intravenous delivery), controlled release and the ability to direct the drug, by various means, to where it is needed.

- **Medical implants and new organs.** In the longer term there is the potential to produce longer lasting medical implants and to even grow new organs using nanotechnology. This will result from the ability to produce stronger structures and to produce surface properties designed to encourage or discourage cell growth or increase biocompatibility.

The above list of applications is by no means exhaustive, but it shows how broad is the current use of nanomaterials and some of the potential new areas of application. Proposals for new areas of application are being regularly reported in the scientific literature. Predicting the timescale for commercial development is very difficult. For some, development is much faster than anticipated, while for others it takes longer or commercial development is abandoned because the method is too costly, is not practicable, or the work is overtaken by new developments that offer a better way of achieving the same goal.

2.2 PRODUCTION TECHNIQUES

There are two basic approaches to the production of nanomaterials. The first is the ‘top-down’ approach, which involves the breaking down of the bulk material into nanosized structures or particles. These techniques are an extension of those that have been used for producing micron-sized particles. An example of such a technique is high-energy wet ball milling. Often an abrasive is added to the process to aid the milling process and milling times can vary from several hours up to many days. In general, increased energies and milling times result in decreased particle sizes. An alternative technique is cryogenic milling, where the material is first cooled to a low temperature to make it more brittle and easier to break down by milling. The difficulty with top-down approaches is ensuring all the particles are broken down to the required particle size. Milling typically results in a Gaussian size distribution with a long ‘tail’ representing the un-milled product. Furthermore, longer milling times will result in more milling impurities, which together with any milling aids, if used, can be difficult to remove.

The alternative approach, which has the potential of creating less waste and hence is more economical, is the ‘bottom-up’ approach. In this approach individual atoms or molecules are built up to form the require nanostructure or nanoparticles. Many of these techniques are still under development or are just beginning to be used for commercial production of nanopowders. The major technical difficulties to overcome in developing a successful bottom-up approach is controlling the growth of the particles and then stopping the newly formed particles from agglomerating. Other technical issues are ensuring the reactions are complete so that no unwanted reactant is left on the product and completely removing any growth aids that may have been used in the process.

Bottom-up approaches, in current use or at an advanced stage of development, can be classified into liquid, vapour or solid phase techniques.

2.2.1 Liquid phase techniques

Wet chemistry techniques that have been used for producing larger particles are being adapted to produce nanosized material, the product crystallising or precipitating out of the solution. In order to achieve the reduction in particle size the reaction chemistry must be chosen to provide a fast spontaneous reaction and also be able to limit subsequent growth of the particles after

nucleation. The particle size can be controlled by the use of various polymers, gels or microemulsions to constrain the growth of the particles.

An example of a liquid phase technique is the Sol-Gel process⁴. This process is used for making ceramic nanomaterials and involves converting from a liquid ‘sol’ phase (mainly colloidal) to a solid ‘gel’ phase. Depending on the subsequent treatment of the ‘gel’ phase, ultra fine or spherical shaped powders, thin film coatings, or ceramic fibres, amongst other products can be produced.

2.2.2 Vapour phase techniques

There are a number of techniques that can be classed under this category, but they all involve two basic steps. The first step is the vaporisation of the material followed by a rapid controlled condensation to produce the required size of particle. In some techniques the powder formed is the same composition as the starting material, while others rely on decomposition occurring during the vaporisation step to produce the desired product.

Production of carbon black, obtained by collecting the soot produced by the burning of natural gas or other hydrocarbons, is probably the earliest example of a vapour phase technique. Silica (silicon dioxide) and titanium dioxide are also produced in bulk by a combustion (flame synthesis) process. A modification of the flame synthesis, known as sodium flame and encapsulation (SFE) technology⁵, is currently under development, which should also allow the bulk production of non-oxide powders of ceramics, metals and composites. In SFE the particles are encapsulated as they formed by a protective layer, which prevents oxidation and inhibits agglomeration.

Other energy sources besides combustion are now being used to vaporise the material. For example metal nanopowders can be produced by an exploding wire technique. This technique is applicable to any metal that is available as a continuous ductile wire⁶. Diamond nanopowders are being produced by a detonation process⁷. Metal, metal oxide and ceramic nanopowders are being produced using a plasma arc to generate the vapour^{8,9}. An electromagnetic vaporisation process (EVP)¹⁰, using an alternating magnetic field to generate fine droplets of molten metal, is being used to produce metal nanopowders. Yet another variant is laser ablation¹¹. In this technique a high-energy laser beam is used to evaporate a compressed precursor powder. The evaporated material is then condensed into nanoparticles by a process of collision and growth. Development work continues on all of these techniques to increase their yields and reduce the production costs.

2.2.3 Solid phase techniques

An example of this technique is mechanochemical processing (MCP)¹² that is being used to produce metal oxide nanopowders. Dry milling is used to induce chemical reactions through ball-powder collisions that result in nanoparticles being formed within a salt matrix. The particle size produced depends on the chemistry of the reactant mixture, milling and heat treatment conditions. Particle agglomeration is minimised by the salt matrix, which is then removed by a simple washing procedure.

2.3 MATERIALS AND QUANTITIES

Materials currently being produced as nanopowders include: metals; metal oxides, borides, carbides, nitrides and sulphides; and, non-metal materials such as various forms of carbon, clay silica and silicon carbides. Most nanopowders are usually produced in spherical form, but nanosized particles can also be produced as flakes (eg aluminium), fibres (eg Teflon and other

polymers) or tubes (eg carbon nanotubes). In the case of fibres and tubes the lengths can fall well outside the nanoscale. For example carbon nanotubes can be produced with diameters down to 1 nm, though the lengths can be up to 1 mm.

The literature search found little information on the quantities of nanopowders that are produced or used by industry. What is known is that the production and use of the nanopowders that have an established use, eg materials like carbon black, silica, titanium oxide and zinc oxide, is in tonne quantities. While at the other end of the scale for some of the more exotic materials that are now being produced as nanopowders, the amounts being produced and used are no more than gramme quantities.

Many of these materials if finely divided with particle sizes in the micron-range and dispersed in air can form explosive clouds. The expectation would be these materials would, given the right conditions, be also capable of forming explosive dust/air clouds with nanosized particles.

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3 DUST EXPLOSION HAZARDS

Explosive dust clouds can be generated from most organic materials, many metals and even some non-metallic inorganic materials. Dust explosions involving particle sizes ranging from a few microns (one micron (μm) is equivalent to 10^{-6} m) to hundreds of microns have been extensively studied. For a comprehensive review of the current understanding of dust explosions, including explosion prevention and protection methods, see Eckhoff³.

The primary factor influencing the ignition sensitivity and explosion violence of a dust cloud is the particle size or specific surface area (ie the total surface area per unit volume or unit mass of the dust). 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 ignition to increase as the particle size decreases, though for many dusts the trend begins to plateau at particle sizes of the order of tens of microns (μm). No lower particle size limit has been established below which dust explosions cannot occur.

3.1 EFFECT OF PARTICLE SIZE

At least for particles in the micron-size range the particle size has a marked effect on the explosion severity and the ease of ignition. The general trend is for the explosion severity to increase and the LEL and ignition energy to decrease. The relationships with particle size are not linear and for some of the parameters the effect plateaus at the smaller particle sizes studied.

For coal Eckhoff³ reports that the limiting particle size, below which there is no further increase in the maximum explosion pressure or the rate of pressure rise, is about 50 μm . The reported data covered particle sizes ranging from about 30 to 150 μm . Over the range 50 to 150 μm the measured maximum explosion pressure and maximum rate of pressure rise increased from about 7.5 to 9 bar and from about 20 to 130 bar/s respectively. Peukert⁴ gives a plot of maximum explosion pressure versus particle size for methylcellulose, polyethylene, PVC and flour, covering particle sizes ranging from about 30 to 400 μm . The maximum explosion pressure plateaus at a particle size of roughly 50 μm for flour, about 40 μm for methylcellulose, and polyethylene, but shows no sign of 'plateauing' for PVC.

The reason for a limiting particle size can be explained if one considers the various steps in the reaction mechanism. In the case of a dust explosion involving coal, or any other organic material, pyrolysis or devolatilisation always precedes combustion, which primarily occurs in the homogeneous gas phase. The limiting particle size, below which the combustion rate of the dust cloud ceases to increase, depends on the ratios between the time constants of the three consecutive steps of devolatilisation, gas phase mixing and gas phase combustion. Particle size primarily influences the devolatilisation rate – a higher specific area allowing faster devolatilisation. Therefore, if the gas phase combustion is the slowest of the three steps, increasing the devolatilisation rate by decreasing the particle size will not increase the overall combustion rate. For materials yielding gaseous pyrolysis products that are more reactive than the volatiles from coal, one would expect the limiting particle size to be smaller than for coal, which turns out to be the case. Natural organic products, such as starch and protein, have a limiting particle size of the order of 10 μm and for reactive dusts like organic dyes it should be even smaller.

For metal dusts, especially the more reactive metals like aluminium and magnesium, the limiting particle size should be even smaller than for organic dusts. No limiting size data could

be found in the literature, but a plot of rate of pressure rise against specific surface area for aluminium¹³ shows the rate still increasing at a specific surface area of 6.5 m²/g. This would correspond to mono-sized spherical particles of 0.34µm in diameter. The reason for the lower limiting size is that the reaction steps for a metal dust explosion are different and thus the rate limiting step will be different. Metal particles do not devolatilise or pyrolyse, but melt, evaporate and burn as discrete entities.

The variation of lower explosion limit (LEL) with particle size also exhibits a plateau. The LEL is taken as the lowest dust concentration at which an ignition can be achieved (see 3.2.1). A plot given by Eckhoff¹³ shows for low volatile coal the limiting particle size is about 20 µm (LEL of about 150 g/m³), for high volatile coal about 50µm (LEL of roughly 130 g/m³) and for polythene about 80 µm (LEL of roughly 50 g/m³). It should be noted that the limiting particle size at the LEL is not necessarily the same as the limiting value obtained at higher dust concentrations, where the explosions are more violent.

The limiting particle size, at which the influence on the LEL begins to plateau, also shows a dependence on oxygen concentration. For coal¹³, reducing the oxygen concentration from the 21% in air to 15.5% reduces the limiting particle size from about 50 µm to 15 µm. Increasing the oxygen content to 50% increases the limiting particle size to about 100 µm. As would be expected the actual value of the LEL decreases as the oxygen concentration is increased.

The available data¹³ on the influence of particle size on the minimum ignition energy (MIE), ie the minimum energy required to ignite the dust cloud (see 3.2.3), indicates a very strong dependence, a near exponential relationship, with no obvious 'plateauing' of the relationship even at particle sizes down to a few microns. A theoretical treatment developed by Kalkert and Schecker¹⁵ predicts that the MIE is proportional to the cube of the particle diameter. Experimental results given in Eckhoff¹³ for polyethylene powder are in agreement with this predicted relationship. The polyethylene data covers a particle range of 25 to 250 µm – the MIE increasing from 10 to 3000 mJ over this range of sizes. For comparison purposes the MIEs of stoichiometric hydrocarbon/air mixtures are typically of the order of 0.25 mJ.

Electrostatic charges can build-up on powders during transport, handling and processing. The charging tendency of highly insulated powders observed in industrial operations does not depend much on the composition of the powder, but more on the operations performed and the specific surface area of the powder¹⁶. The charging tendency has been found to drastically increase with increasing specific surface area. For example log-log plots of charge to mass ratio vs specific surface area for various organic powders show a near linear relationship. Nanopowders, because of their large specific surface areas, may well become highly charged in use and thus be their own ignition source if the powder is dispersed to form an explosible cloud.

In practical applications, at least for micron-scale powders, there is usually a wide distribution of particle sizes within the powder. The influence of particle size will be less marked than the above relationships suggest, which were obtained with near mono-sized distributions (narrow range of particle sizes).

3.2 OTHER FACTORS

There are other factors, which determine whether a dust cloud can be ignited and the violence of the resulting explosion. The main ones are discussed below.

3.2.1 Dust concentration

Dusts, like gases and vapours, can only form explosive clouds if the dust concentration lies between certain limits, known as the lower explosion limit (LEL) and upper explosion limit (UEL). For dusts the LEL is sometimes referred to as the minimum explosive concentration (MEC). The explosion limits for dusts are not as well defined as for gases and vapours, particularly the upper limit. Actual values will depend on the dust composition, the particle size distribution and the method of determination, but typical values are around 50-100 g/m³ for the lower limit and 2-3 kg/m³ for the upper limit.

3.2.2 Dust composition

If the dust is not combustible or reactive with the surrounding gaseous atmosphere there cannot be a dust explosion.

3.2.3 Ignition strength

The ignition energy must be high enough to ignite the dust particles. The parameter usually used as a measure of the ease of ignition of a dust cloud is the minimum ignition energy (MIE), which is defined as the lowest electrical energy stored in a capacitor which upon discharge is sufficient to ignite the most easily ignited dust cloud. Values for dusts are typically in the range of 1 to 10 mJ.

3.2.4 Degree of dust dispersion

Dispersion and degree of agglomeration affect the combustion as they change the effective local dust concentrations and the effective particle size respectively. A more evenly dispersed dust will burn more easily. The degree of dispersion is usually dependent upon the way the dust is dispersed and the level of turbulence in the dust cloud.

3.2.5 Initial conditions

Increasing the initial temperature lowers the ignition energy and the LEL. The maximum explosion pressure, however, decreases, as the air density is lower and thus the mass of oxygen available for reaction is lower. Increasing the initial pressure increases the explosion pressure, due to the increased air density, and lowers the ignition energy. Increasing the turbulence of the dust cloud will increase the rate of reaction and thus the rate of pressure rise. The effect of turbulence on the maximum pressure is less marked. A less turbulent dust cloud is more easily ignited, as the energy input from the ignition source is dissipated at a lower rate, the initial energy input more locally concentrated, leading to a higher probability of ignition for a given energy input.

3.2.6 Oxygen content

Less oxygen in the air reduces the explosion severity, as it limits the rate of combustion of the dust, and increases the ignition energy. On reducing the oxygen content of the air by diluting with an inert gas, such as nitrogen or carbon dioxide, an oxygen concentration is reached below which the explosion is completely suppressed. This oxygen concentration is known as the limiting oxygen concentration (LOC). Typical values for organic dusts range from about 11 to 15% v/v. Suppression of a dust explosion by inerting is, however, mainly due to the inert gas acting as a heat sink and quenching the explosion rather than due to the reduction in the rate of combustion. Thus the LOC for a particular dust does depend on the inert gas used. Inerting is

more efficient, that is a higher LOC value, for inert gases with a high heat capacity.

3.2.7 Moisture and solvent content

The moisture content of the dust will affect the ease of ignition and its ability to sustain an explosion. Increasing the moisture content increases the ignition energy, for some dusts the increase can be exponential, and reduces the explosion violence (the water vapour produced acting as an inert heat sink). The presence of a flammable solvent on the dust will have the opposite effect, lowering the ignition energy and possibly increasing the explosion violence.

3.2.8 Hybrid mixtures

These are mixtures of dusts and flammable gases or vapours. The presence of a flammable gas or vapour can increase the explosion severity and reduce the ignition energy, even when the concentration of the gas or vapour is below its LEL. Hybrid mixtures can also be explosive when both the concentration of the dust and the gas or vapour is below their respective LELs.

3.3 EXPLOSION CHARACTERISTICS OF NANOPOWDERS

A preliminary search of the literature has found only one reference giving data on the explosion characteristics of a nanopowder. For an aluminium nanopowder, with a reported mean particle size of 180 nm, a maximum pressure of 9.4 bar, K_{St} of 322 bar m s⁻¹, MIE of 1-3 mJ and LOC of 5% was measured¹⁷. A 20 litre sphere apparatus and standard procedures were used for these measurements. The values for the maximum pressure and K_{St} are lower than the reported values¹⁶ for aluminium powders with a median particle size of tens of microns, the MIE value is higher and the LOC comparable.

On the basis of this one result it could be concluded that the explosion hazard from aluminium nanopowders is less than that from coarser micron-sized aluminium powders. Such a conclusion should be viewed with caution, for a number of reasons other than the obvious one that it is just based on one result. First though the aluminium powder tested contained particles with dimensions of nanometres, the range of particle sizes falls outside the usual definition of nanopowders as having particle sizes in the range of 1 to 100 nm. Second the surfaces of metals like aluminium can readily oxidise when exposed to air, which reduces their reactivity. Thus if oxidation occurs before the explosion characteristics are measured, the result will be low values of the maximum explosion pressure and K_{St} . Finally very fine particles can readily agglomerate into what are effectively larger particles, which also reduces their reactivity. It is thus possible that the standard method of dispersion employed in the 20 litre test apparatus did not ensure adequate dispersion and some agglomeration of the particles occurred before ignition.

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 behaviour of the particle surface starts to determine the behaviour 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. At the micron scale metal oxide dusts are not explosible¹⁸. It is possible that at the nano-scale metal oxides could react to give a higher oxidative state and thus become explosible. This is purely speculative at this stage, as no evidence has been found in the literature that this can occur. Similarly mechanisms can be postulated that could lead to dusts that are explosible at the micron-scale becoming non-explosible at the nano-scale. For example if the oxide layer on metal particles remained at the same thickness, the amount of metal remaining for combustion would decrease as the particle size decreased. This could in the very least reduce the explosion violence, or in the extreme

reduce the metal content to such an extent that an explosion could not occur. If, however, the oxide layer became reactive at the nanoscale this could offset the effect of the reduced metal content. In conclusion, without supporting experimental data it would be unwise to assume that a nanopowder is explosible or not based on the behaviour of the powder at the micron-scale.

Another factor to bear in mind in assessing the explosion hazard from nanopowders is that these powders tend to be produced with a fairly narrow size range. The effect of particle size is likely to be much more marked, than a powder with a broader size distribution - the larger, less reactive particles, countering the increased reactivity of the smaller particles.

The expectation would be that nanopowders are more easily ignited than a coarser powder of the same material. There are no experimental measurements of ignition energies to back up this assertion. Consistent with easier ignition is the fact that some nanopowders are pyrophoric, that is they spontaneously ignite when exposed to air. An example of a pyrophoric nanopowder is iron.

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 non-explosible at the micron-scale.

3.4 OTHER CONSIDERATIONS

In order to have a dust explosion as well as the dust having to be explosible and an ignition source present there must be some means of first dispersing the powder in air, or other gaseous medium with which it can react, at a concentration within the explosive range. Clearly if this cannot occur then there is no risk of an explosion occurring. For example if the powder is manufactured by a wet process and is subsequently handled and stored dispersed in a liquid it is unlikely to form a dust cloud. If the powder is wetted with a liquid then the chances of it forming a dust cloud are also low.

The drying of powders can both produce a dust cloud and also provide an ignition source for the dust cloud. For example in a rotary drier a dust cloud will be generated within the drier. Even if the dust concentration in the drier is above the upper explosion limit during normal operation, the concentration will pass through the explosive range during start-up and shutdown. If the drier temperature is too high or the residence time in a drier is too long there is also the risk of dust accumulations in the drier beginning to smoulder, or even burst into flame. The smoulder or burning dust can then be the ignition source for a dust explosion within the drier and connected plant.

Given a dry powder there are a number of ways in which it can become dispersed to form a dust cloud. The handling and transport of powders, for example pouring powders from a storage container into a vessel, can generate a dust cloud. Airflow across a dust deposit, especially one composed of fine particles, can also generate a dust cloud by erosion of dust particles from the deposit surface. One of the classic ways in which a dust explosion can occur is by a small primary explosion, which does not necessarily have to be a dust explosion, raising dust from a deposit. The resulting secondary explosion of the raised dust lifts further dust from the deposit, providing further fuel for the explosion. Depending on the extent of the dust deposit a very powerful secondary dust explosion can result from a small weak primary explosion. This is the reason why good housekeeping, to prevent the accumulation of dust deposits in and around equipment and plant, is so important.

For ignition of a dust cloud to be possible then the dust concentration has to be between the lower and upper explosion limits. For micron-scale dust clouds the dust particles will settle out, so dust concentrations initially above the UEL can quickly fall within the explosible range and then below the LEL. The period over which an explosion can be initiated is, therefore, relatively short. As a rough rule of thumb particles below about one micron can be considered to remain airborne for long periods of time, with minimal fall out of the dust. The concentrations of dust clouds of nanopowders are thus likely to remain fairly steady for long periods of time, unless some corrective action is taken to disperse or remove the dust from the air. This in turn means that the risk of an explosion from a nanopowder cloud could also persist for much longer than a cloud of the same material composed of micron-scale particles.

Dust handling systems are often designed to operate at concentrations above the UEL, eg pneumatic pipelines for conveying the dust into storage bins. In assessing the explosion hazard of these systems account needs to be taken of the possibility during start-up or shutdown of the dust concentration passing through the explosive range.

Agglomeration can be a problem, especially for very fine powders. Considerable effort is devoted in the manufacture and use of nanopowders to eliminate agglomeration, otherwise the very properties that required their use in the first place would be changed. Little information could be found on how agglomeration would affect the properties of nanopowders. It would certainly reduce the specific surface area and as a result the reactivity of the powder would be expected to be lower. The experience with micron-scale dusts is that agglomeration results in explosion characteristics that are comparable to dusts with particles of the same size as the agglomerated particles. To ensure the explosion characteristics of nanopowders are correctly measured it is important that agglomeration does occur when the powder is dispersed in the test apparatus. Failure to prevent agglomeration could result in the explosion hazard being underestimated.

Another consideration that is particularly relevant to nanopowders is the quantity of powder being handled. For cost reasons, limitations of current manufacturing methods or the particular application many nanopowders are produced or used in small quantities (gramme quantities). The explosion hazard from such small amounts of material will be negligible. At present only those nanopowders that have a well established use, are manufactured in reasonable quantities and are handled dry are likely to give rise to a dust explosion hazard, eg carbon black. As manufacturing methods improve and demand for nanopowders grows an increasing range of materials are likely to present an explosion hazard.

4 CONCLUSIONS AND RECOMMENDATIONS

1. An increasing range of materials that are capable of producing explosive dust clouds are being produced as nanopowders. At the same time new uses of nanopowders are further adding to the demand for these powders. While some of these nanopowders are only being produced in very small quantities at present, and may continue to be for the foreseeable future, the production of others is likely to increase significantly over the next few years.
2. There is a growing concern over the impact the increased use of nanopowders and other nanomaterials will have on health and safety and the environment. These concerns are almost exclusively centred on the potential toxic effects of nanomaterials. The potential explosion hazards of nanopowders have not been addressed.
3. There is a considerable body of knowledge on the explosion characteristics of micron-scale powders (particle sizes ranging from about 10 to 500 μm). A literature search has found no data for nanopowders (particle sizes of 1 to 100 nm). It is considered that the extrapolation of the data for larger particles to the nano-size range cannot be carried out with any degree of confidence, due to marked change in the chemical and physical properties of particles below sizes of about 100 nm.
4. It is recommended that the explosion characteristics of a representative range of nanopowders be determined using the standard apparatus and procedures already employed for assessing dust explosion hazards. Comparison with data for micron-scale powders of the same materials will allow knowledge of particle size effects to be extended into the nanosize range.
5. Although it is recommended using standard apparatus and procedures for measuring the explosion characteristics of nanopowders, if agglomeration is thought to be occurring in the test vessel it may be necessary to modify the way the powder is dispersed. This is to ensure that the worst case characteristics will be measured.

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