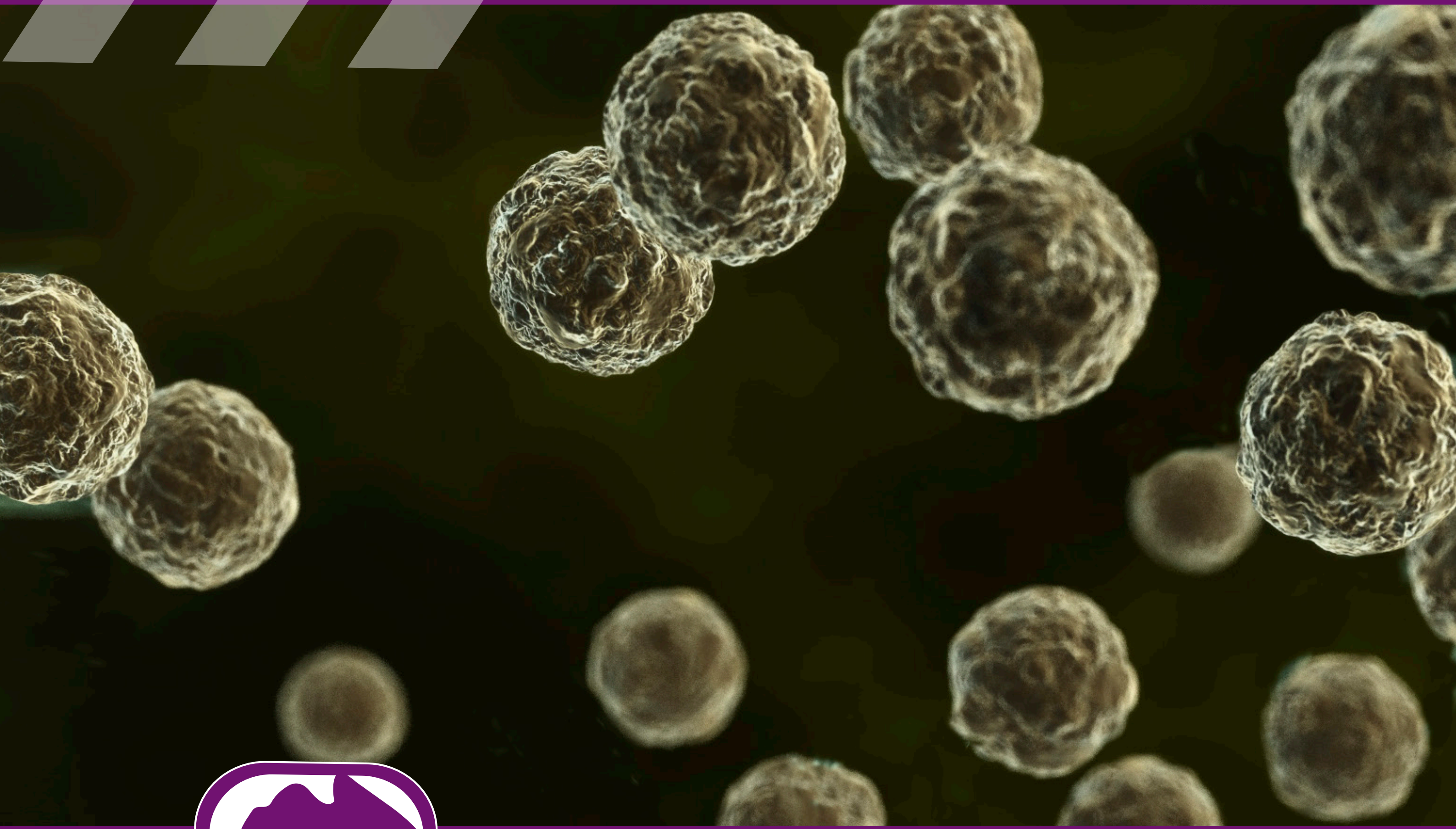
EVALUATION OF POTENTIAL SAFETY (PHYSICOCHEMICAL) HAZARDS ASSOCIATED WITH THE USE OF ENGINEERED NANOMATERIALS



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Evaluation of potential safety (physicochemical) hazards associated with the use of engineered nanomaterials.

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Executive summary

This review was produced by Toxikos Pty Ltd under commission from Safe Work Australia through funding provided under the National Nanotechnology Strategy. It reports the current understanding of the safety (physicochemical) hazards associated with engineered nanomaterials (ENMs), and the implications in regard to hazard assessment during manufacture, handling, transport and use. The review only considers ENMs present as a nanoparticle or a nanofibre i.e. nano-objects, it does not consider nanomaterials fixed or embedded within a matrix. The information in this review is based on scientific literature and overseas governmental reviews published up to November 2011.

A key objective during the preparation of this review was to consider published information for ENMs (particle size range 1-100nm approximately) and assess whether they behave differently with respect to physicochemical hazards than the equivalent microfine material i.e. material with at least one dimension in the micron range (μm) and none smaller. However there was a lack of information (i.e. test data) to provide a meaningful discussion on most of the hazard categories for physicochemical hazards as provided within the Globally Harmonized System of Classification and Labelling of Chemicals (GHS 2009) and the Australian Dangerous Goods Code (NTC 2007). In particular this applied to the hazard categories of explosivity specifically related to explosive substances, corrosivity to metals, oxidation, pyrophoric substances and self-reactive or self-heating substances.

While there are general safety hazards associated with the use of nanomaterials, e.g. associated with the risk of electrocution and asphyxiation, these are not examined in this report which focuses on the safety hazards arising directly from nanomaterials' physicochemical properties. Available test data related to physicochemical hazards of ENMs in the general literature is primarily associated with combustibility and explosivity of dusts. The potential for a dust cloud to explode is articulated as a primary concern, and this report examines whether, due to their increased surface area, ENMs may result in explosions that are proportionally more severe than those observed for microfine materials. It is important to note that a mixture (i.e. dust cloud) that has the potential to ignite and result in an explosion is not a criterion for classifying the material as an explosive substance using the classification system in the GHS or ADG Code.

Predictions regarding the explosive potential of ENMs are uncertain for a number of reasons. Firstly there is limited data spanning the particle size range of interest and only relatively few ENMs have been investigated. Secondly, the comparisons with bulk microfine materials performed in this review relied on test results that are not easily compared because they come from a variety of different sources. These research investigations used modified, non-standardised test equipment to overcome testing difficulties associated with ENMs that are not encountered with microfine dusts. There is however information for the pivotal explosive properties of Minimum Explosive Concentration (MEC), Minimum Ignition Energy (MIE) and the maximum rate of pressure rise (R_{max}).

It was found:

- A reduction in MEC occurs for microfine materials with a reduction in their particle size. However, the MEC reaches a threshold in the micrometre size range, below which no further decrease is observed. Therefore for ENMs, the MEC is independent of their size but is determined by the nature of the ENM. Importantly, the mass concentration of ENMs in a dust cloud needed for an explosion is orders of magnitude in excess of air levels measured for ENMs in a well-managed workplace. However there are specific situations where the MEC may be exceeded, e.g. where production processes are not designed and/or controlled effectively or where handling processes are involved. It should also be appreciated that ENMs tend to stay airborne for considerably longer periods of time when compared to their micron sized counterparts.

- For microfine materials a reduction in particle size decreases the energy required to ignite the dust cloud (i.e. MIE decreases). This trend appears to continue into the nanoscale however data is insufficient for confirmation. Nonetheless, it is apparent that ENMs can be very sensitive to ignition when their microfine material counterparts are also ignitable, i.e. ENMs are more easily ignited than their microfine counterparts when they themselves are easily ignited.

- The severity of explosion (indicated by R_{max}) for ENMs is potentially less than that seen for microfine material counterparts. This is based on the following R_{max} data for microfine and nanomaterials:
    1. A rapid increase in the magnitude of R_{max} occurs with decreasing particle size for microfine materials. However this effect peaks at about 3μm.
    2. Below approximately 0.3μm the available data indicates the opposite trend may occur, i.e. there is potentially a sharp decrease in R_{max} with decreasing particle size for ENMs.

3. The potential for the highest R_{max} values (and therefore most severe explosions) occurs for particle sizes between approximately 0.1μm and 10μm.

It might be anticipated from their increased surface area that the explosion severity of ENMs may be proportionally worse than that with microfine dust clouds of similar suspended mass. However the information above indicates this may not be the case. From the literature for explosivity of dust clouds it appears ENMs do not represent a unique safety hazard due to their very small size. It should be noted however that some ENM dust clouds are still able to result in very strong explosions if dust concentrations are sufficiently high.

Thirty four of the Safety Data Sheets (SDS) assessed in *An Evaluation of MSDS and Labels associated with the use of Engineered Nanomaterials* (Safe Work Australia 2010) were revisited for this review. In general, for the ENM SDSs reviewed, there was a lack of information provided to enable workers to identify safety hazards associated with the use of ENMs. Information related to dust explosions were typically sourced from their bulk counterparts, if supplied at all. There is also the possibility that SDS may not be supplied for ENMs when the chemical/substance is not already classified as hazardous in bulk form. There is therefore an implication that hazards associated with ENMs may not be suitably identified in the workplace. This situation may improve following the publication of the evaluation and information on nanomaterials in the model Code of Practice on *Preparation of Safety Data Sheets for Hazardous Chemicals* (Safe Work Australia 2011).

With regard to workplace implications, the dearth of data makes it difficult to draw general conclusions about the physicochemical safety aspects of ENMs that are related to their nano-size characteristic. It is nonetheless recognised the explosive behaviour of airborne ENMs is different to their microfine material counterparts; some may be more easily ignited but the explosion severity is not expected to be worse. The air concentrations of ENMs required for an explosion appear to be much higher than will be found in a well-managed workplace as a result of fugitive emissions from processes that involve nanotechnology. However, in the situations where production is not designed and/or controlled effectively, in processes (e.g. grinding of materials) or in handling there is potential for air concentrations in localised area to result in explosion.

Notwithstanding the above, it is prudent:

- For ENMs to be assessed for explosivity on a case by case basis, preferably using standardised, validated test methods.

- In the absence of specific information, to assume dust clouds of all ENMs present an explosion hazard.
- For precautionary information regarding explosivity to be provided on safety data sheets irrespective of whether bulk chemical is classified as explosive.

There is capability within Australia to perform dimensional measurements on ENMs. Internationally the measurement of explosion parameters for ENMs is undergoing development and two laboratories were found in Australia with the capability to measure these properties.

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1. Introduction

This review reports on the potential safety (physicochemical) hazards associated with use of engineered nanomaterials (ENM) and the implications in regard to hazard assessment during manufacture, handling, transport and use. An ENM is a particle, fibre or plate with at least one dimension of size range 1 to 100 nanometres (nm). The safety hazards of ENMs fixed or embedded within a matrix are not considered in this report.

As a result of concerns regarding manufacture, use and disposal of ENMs there has been significant research around the world directed towards understanding potential health and environmental impacts. Relatively little effort has been directed towards safety aspects of ENM that are dependent on physicochemical properties.

The review was commissioned by Safe Work Australia and is based on literature published up to October 2011. Specific objectives of this review on the safety hazards of ENMs are to:

- present and evaluate research results reporting potential safety (physicochemical) hazards
- identify gaps in current knowledge
- report on the current capability for testing engineered nanomaterials for physicochemical hazards within Australia
- review information regarding the suitability of current test methods
- identify engineered nanomaterials used in Australia which may require physicochemical hazard testing to be performed, and the specific tests which need to be undertaken, and
- evaluate implications for the protection of health and safety in the workplace.

In essence the review considers the published information for ENMs and whether they will behave differently with respect to physicochemical hazards than the equivalent microfine material or bulk material because of their nano-scale. It considers whether current classification systems and hazard categories based on the physiochemical properties of bulk materials are suitable for application to nanomaterials. The hazard categories considered are those specified within the Globally Harmonised System of Classification and Labelling of Chemicals (GHS 2009) and include; explosivity, flammability, corrosivity to metals, oxidation, and pyrophoric, self-reactive or self-heating substances, and substances which in contact with water emit flammable gases.

There are general safety hazards associated with the use of nanomaterials, e.g. associated with the risk of electrocution and asphyxiation, but these are not examined in this report which focuses on the safety hazards directly arising from nanomaterials' physicochemical properties. Information on these general hazards has previously been reported (ISO 2008b).

2. Current categories for physicochemical hazards

In Australia, under the Work Health and Safety Regulations (WHS 2011), workplace hazardous chemicals are classified according to the GHS. For the purposes of transport, Dangerous Goods are classified according to the *Australian Code for the Transport of Dangerous Goods by Road and Rail* (the ADG Code) [1]. The latest edition of the ADG Code is the 7th edition.

For workplace health and safety regulations in Australia a hazardous chemical refers to ***"****a substance, mixture or article that satisfies the criteria for a hazard class in the GHS"* (with a small number of changes as noted in the Work Health and Safety Regulations, WHS 2011). The same physical hazards covered in the GHS are also covered by the ADG Code.

Relating to safety hazards, an outline showing the provenance of the Commonwealth, State and Territory work health and safety legislation and dangerous goods transport legislation is summarised in Figure 2.1.

The WHS and transport regulations apply to chemicals during transport, storage and use, regardless of physical form (i.e. gas, solid or liquid) and irrespective of whether they are physically contained or are airborne as aerosols or dusts. Thus conceptually the criteria underpinning the hazard categories in the dangerous goods regulations should be useable for assessing the physiochemical safety hazards of ENMs, since ENMs can be regarded as an ultrafine form of the bulk substances for which the regulations were designed.

The UN Model Regulations and subsequently the ADG Code are based on classification criteria agreed during the development of the GHS. The third revised edition was published by the UN in 2009 (GHS 2009) and this edition is specifically referenced in WHS Regulations. The fourth revised edition was published in 2011. The development of the physicochemical hazard criteria was carried out under the auspices of OECD for health and environmental effects and the UN Committee of Experts on the Transport of Dangerous Goods.

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[1] The Commonwealth Department of Infrastructure, Transport, Regional Development and Local Government is responsible for maintaining the ADG Code through which requirements for the land transport of dangerous goods in Australia are harmonised. The ADG Code is closely aligned with international requirements for the land transport of dangerous goods (TDG), in particular the UN Recommendations on the Transport of Dangerous Goods - Model Regulations (UN Model Regulations).

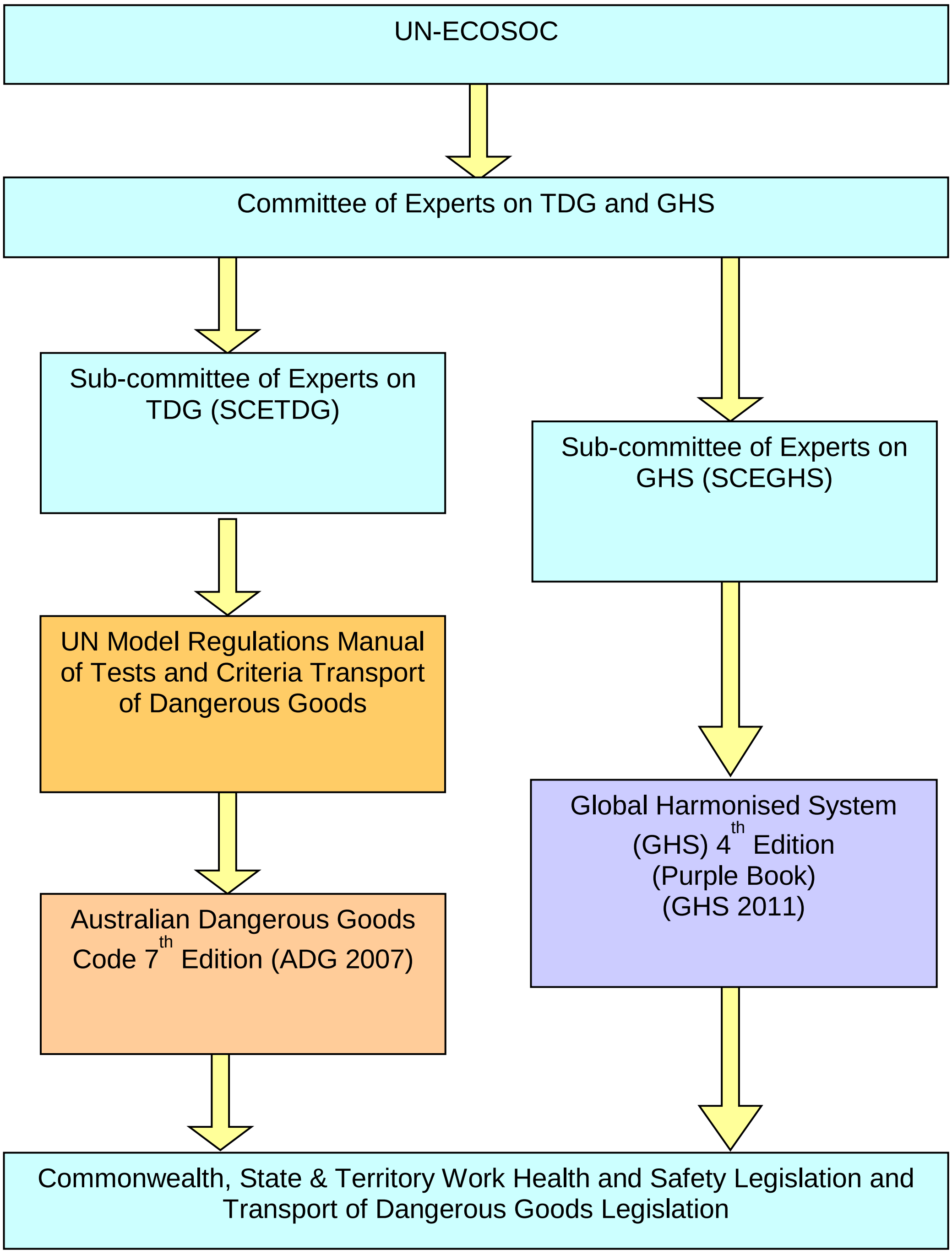

Figure 2.1: An outline of the provenance of legislation relating to safety hazards governed by a substance's physicochemical characteristics.

ECOSOC = Economic and Social Council
TDG = Transport of Dangerous Goods
GHS = Global Harmonised System

2.1 Potential physicochemical hazards of ENMs.

The safety hazards of substances in the workplace that are not nanomaterials have been recognised from many decades of experience and testing. Over this time classification criteria have been developed that are integrated into the workplace and are used to inform engineering designs for mitigating the risks associated with the hazards. These criteria are embodied in the Australian Dangerous Goods (ADG) Code and the GHS. Therefore, an obvious approach for identifying the physicochemical properties of ENMs that may present safety hazards in the workplace is to evaluate the hazard classification criteria associated with substances currently used in the workplace for their applicability to ENMs.

The UN model regulations for the transport of dangerous goods, the Australian Dangerous Goods code and the GHS criteria are essentially the same with respect to physicochemical hazard classification. The following physicochemical properties are identified in these documents as safety hazards and are assessed in this review. It is noted however that for most of these properties there is insufficient data for ENMs to allow a meaningful comparison with their micro-sized counterparts. Consequently it is not possible to confidently indicate that the current criteria used for traditional substances to classify or categorise these properties for safety hazard severity are applicable for ENMs. The following sections of this report provide a brief account of the physicochemical hazards as currently described in the ADG and GHS documents. The physicochemical properties used to characterise substances in general are:

- explosivity
- flammability
- emission of flammable gases after contact with water
- metal corrosivity
- pyrophoricity
- oxidising behaviour
- self-heating
- self-reactivity

2.1.1 Explosivity.

An "*explosive substance (or mixture) is a solid or liquid substance (or mixture of substances) which is in itself capable by chemical reaction of producing gas at such a temperature and pressure and at such a speed as to cause damage to the surroundings*" (NTC 2007, GHS 2009). The current classification/criteria for explosivity is specific for the presence of certain chemical groups in a molecule or compound (i.e. reactive oxidising and fuel functional groups) which in the same molecule or compound can react together to produce very rapid increases in temperature and/or pressure. These substances are classified as explosives Class 1, within which they may be separated into six divisions according to the results of three core tests[1]:

- explosivity (e.g. the manner in which a test chamber is punctured or fragments, the time taken to for the pressure in the tube to rise from 690kPa to 2070kPa),
- sensitiveness (e.g. flame is seen or auditory response is heard) and,
- thermal stability (e.g. a measure of an explosive substance to be stored without untoward deterioration).

No information was located that correlated a change in particle size from the micro to nano with a change in explosivity for explosive substances Class 1, i.e. those with an oxidising and fuel functional group.

It is important to note that a specific category does not exist for explosivity of dusts in the current regulations. Substances which can form an explosive atmosphere of gas, vapour or dust are not included in this class of explosive materials. This is a significant distinction to make as the results obtained for explosion severity (to be discussed for ENMs in Section 3) are not used to classify a material as an explosive substance. Rather, testing dusty materials for explosive severity is related to provision of information for their safe use since it has been known from antiquity that certain dusts in air may catch fire and explode. However the technical description of the latter is more an issue of combustibility rather than explosivity as is described for Class 1 substances.

2.1.2 Flammability (solids)

Flammable solids are solids which are readily combustible, or may cause or contribute to fire through friction (NTC 2007, GHS 2009). Readily combustible solids are powdered, granular, or pasty substances which are dangerous if they can be easily ignited (e.g. by a burning match), and if the flame propagates rapidly (GHS 2009), i.e. deflagration. Flammable solids are assigned dangerous goods Division 4.1 dependant on whether a wetted zone stops the fire and retards the burning time or rate.

A number of journal articles and reviews were identified that discuss the effect of reduced particle size on explosivity and combustibility of dusts and ENMs in the workplace. For ENMs the explosion hazard associated with the formation of a dust cloud is highly relevant (Section 3).

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[1] These are the core tests for classing explosive substances into divisions. More tests are necessary for the classification to be performed.

2.1.3 Self-reactivity

Self-reactive substances and mixtures in the context of this review are categorised by their ability to decompose exothermically. The test for self-reactivity uses a standard quantity (50 kg) heated to 75 °C, or lower depending on the Self-Accelerating Decomposition Temperature (SADT).

According to the ADG Code (NTC 2007) the decomposition of self-reactive substances can be initiated by heat, contact with catalytic impurities (e.g. acids, heavy-metal compounds, and bases), friction or impact. The rate of decomposition increases with temperature and varies with the substance. Decomposition, particularly if no ignition occurs, may result in the evolution of toxic gases or vapours.

Self-reactive substances are allocated to Division 4.1 and assigned to one of 7 classes (Type A to G) dependant on the degree of danger they represent. A number of exclusions to this Division include explosives or Class 1 substances, substances in Division 5.1 (with some exclusions), organic peroxides and for substances whose SADT[2] is >75°C for a 50kg package. There was no information identified in the literature that would inform about the relationship between self-reactivity and a decrease in particle size from the microscale to the nanoscale size. Consequently, no conclusions can be made regarding the impact of nanoscaling on self-reactivity.

2.1.4 Pyrophoricity and Self-heating.

Self-heating is the result of an exothermic reaction of a substance or mixture with oxygen in the absence of an ignition source. When a substance is able to generate heat very rapidly[3] it is referred to as a pyrophoric substance.

If the heating occurs slowly[4] the substance is referred to as self-heating. With these substances heat can accumulate with the possible consequence of self-ignition. Pyrophoric substances may ignite even when present in small quantities in a short period of time (i.e. within minutes) whereas for self-heating substances the phenomenon can occur only where a large surface area of substance is in contact with air for a longer period of time (hours or days). Ignition of self-heating substances occurs usually at or near the centre of the substance pile. The substances are assigned to Division 4.2 (NTC 2007, GHS 2009).

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[2] SADT = Self-Accelerating Decomposition Temperature

[3] Ignition occurs for pyrophoric substances within 5 minutes of coming in to contact with air.

[4] Self-heating occurs over a longer period of time (hours to days) and requires large quantities of chemicals.

Information was not located regarding a reduction in particle size on pyrophoricity and self-heating properties of substances down in to the nanoscale. However zirconium powder with a particle size of 3μm was considered extremely pyrophoric compared to a similar powder with a particle size of 12μm (ASM 1998). Hence, based on very limited data, it would appear there is potential for pyrophoricity to increase with a reduction in particle size.

2.1.5 Substances in contact with water emitting flammable gases

These are substances "*which, by interaction with water is likely to become spontaneously flammable or to give off flammable gases in dangerous quantities*" (NTC 2007, GHS 2009). This property is influenced by the chemical structure and/or the physical state (e.g. particle size) of substances. Sometimes this reaction can be violent and/or with significant generation of heat that may initiate a fire. These substances are classified as Division 4.3 if spontaneous ignition takes place or flammable gas is evolved at a rate greater than 1L/kg/h.

Since ENMs are very small particles with large surface area relative to their bulk, it is logical to assume nano-sizing such substances will increase their propensity and vigour for interaction with water. However data to substantiate this assumption were not located. No reports were identified that could link a reduction of particle size to the nanoscale with a change in this property. Consequently, the potential increased propensity and vigour for interaction with water of nanomaterials cannot be quantified at this stage.

2.1.6 Oxidising behaviour (solids)

These are substances able to cause or contribute to the combustion of other materials (NTC 2007, GHS 2009). Certain combinations of combustible materials and oxidising materials may result in spontaneous combustion, thermal instability, or form an explosive mixture. This means they may also be considered for classification based on explosive properties or self-reactivity[5]. Oxidising solids are classified in Division 5.1 based on whether a mixture of the substance and cellulose ignites and burns, or on a comparison of burning time with reference mixtures.

The oxidising properties of a solid depend on its particle size as smaller particles enable more intimate contact between mixture components. The smaller the particle size, the higher the oxidising capability of the solid. As a consequence, it is possible large particles of a certain solid are considered to be non-hazardous, while small particles of the same solid may need to be classified into the hazard class of oxidising solids. However to date studies investigating the physicochemical safety properties of ENMs have not included oxidising properties as part of the

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[5] AS/NZS 4745:2004 Code of Practice for handling combustible dusts.

investigation. Consequently, no conclusions regarding increased oxidising capability or otherwise of ENMs can be drawn at this stage.

2.1.7 Corrosivity (to metals).

These are substances liable to undergo a reaction with metals that leads to significant damage or, in some cases, to full destruction of the metal (NTC 2007, GHS 2009). Consequently a key property with respect to corrosivity is the electrochemical potential of a substance and how this changes with pH. Substances that corrode steel or aluminium at a rate exceeding 6.25mm per year (at 55°C) are considered corrosive to metal and are assigned Class 8.

It may be reasonably anticipated that a reduction in particle size would increase the corrosivity of a corrosive substance due to the higher reactivity associated with the larger surface area of much smaller particles. However no data demonstrating this effect was identified in the literature, nor was information located that investigated, or suggested that a non-corrosive substance would become classifiable as corrosive due to its nano-form. Consequently, no conclusions regarding increased corrosivity or otherwise of ENMs can be drawn at this stage.

2.1.8 Catalytic properties.

Catalysts can change the rate of a chemical reaction while not being consumed by the reaction itself. NIOSH (2009) state that “*some nanomaterials may initiate catalytic reactions that ….would not otherwise be anticipated”.* This comment is attributed to a review by Pritchard (2004). Pritchard (2004) states “*the greater the surface area the more effective a catalyst will be*”, implying that if a substance was innately a catalyst it would be more efficient at small particle size. Pritchard (2004) does not contain information indicating a non-catalyst would become a catalyst by virtue of nano-size. However a review on gold nanoparticles by Daniel and Astruc (2004) suggests a reduction in particle size can lead to the conversion of a non-catalyst to a catalyst. Macro-scale gold is chemically inert, but gold nanoparticles supported on Co_3O_4, Fe_2O_3, or TiO_2 are highly active catalysts, under high dispersion, for CO and H_2 oxidation, NO reduction, water-gas shift reaction, CO_2 hydrogenation, and catalytic combustion of methanol (Daniel and Astruc 2004). The catalytic combustion of methanol is an example which indicates the possibility of a safety hazard.

There are currently no defined physicochemical hazard criteria in the GHS regarding catalysis. Nevertheless, ENMs provide potential for unexpected adverse reactions due to catalysis therefore demanding a precautionary approach when handling ENMs.

Where appropriate the catalytic aspects of ENMs have been considered in this review.

2.2 Summary of nanoparticles and their physicochemical properties

For chemicals, the hazard categories of explosivity, flammability of solids, self-reactivity, pyrophoricity and self-heating, substances in contact with water emitting flammable gases, oxidising behaviour, and corrosivity to metals as outlined in Sections 2.1.1 to 2.1.8 are well defined. For chemical substances there are existing validated and standardised test methods for assessing these properties. To date there have been no specific recommendations by the Expert Committee on Dangerous Goods regarding new test criteria, or test methods for ENMs. It is however recognised that for ENMs, one of the important considerations is identification of physical properties associated with explosivity (HSE 2006) and some information on this has been generated (Section 3). For the other physiochemical properties used to classify the safety hazards of chemicals there is very limited information for ENMs. Hence there is a tendency to extrapolate data on these aspects from microfine materials (HSE 2004a).

Although the validity of such extrapolations remains to be determined, the safety hazards associated with ENMs are assumed to be brought about by increased surface area, hence extrapolation is a reasonable assumption that can be made on precautionary principles.

The absence of classification of an ENM into one of the ADG Code classes does not mean physicochemical hazards are necessarily absent during its use in industrial processes. Industrial processes involving heat, pressure, or mechanical attrition could result in the generation of conditions (e.g. dust, heat, and electrostatic energy) that create a physicochemical hazard. Engineers or operators developing or working with these processes may rely on specific criteria for classifying materials that can result in dust explosions. These criteria are not considered in the ADG Code (NTC 2007), however they are discussed further in this review (see Section 3.6).

Conversely, there are several physicochemical properties associated with the safety classification of chemicals that are not considered further in this review for ENMs. They are not included because there is very little information for ENMs. The information identified in the literature focuses on explosion hazards associated with combustible dust clouds formed during processing and use of ENMs. Materials that are inert in the size range of approximately 10-1000 microns may become highly reactive as ENMs and in air may present a greater safety risk than their 10-1000 micron scale counterparts of a similar composition. For example, the explosion risks of some metals increase significantly with a decrease in particle size in the microscale range (Pritchard 2004, NIOSH 2009).

Due to limited information, this review is only able to provide a discussion for extrapolation of data from microfine materials to ENMs that relates to dust explosion and its severity. Although this data is currently not used for dangerous goods classification (due to the absence of classification criteria for dusts), it provides important insight for the potential safety hazards associated with manufacture and use of ENMs.

3. Combustible dusts

3.1 Introduction

The GHS has classification criteria for flammable solids that are readily combustible solids. However it does not contain classification criteria for the hazards associated with clouds of combustible dusts and , there is no guidance within the GHS regarding what specific information should be included on a SDS for these combustible dusts. The SDS is a primary tool for occupational hazard and risk communication and assessment (e.g. AS/NZS 4745:2004). This section considers the information that is currently available for defining combustible dusts and how it may apply to ENMs.

Over the last two or more decades considerable attention has been paid to the hazard of combustible dust-air mixtures in the manufacturing environment. Dust explosions triggered by a spark or flame have resulted in loss of life and serious damage to plants and buildings. The tests used to determine measures of explosivity have undergone modification for microfine dust materials and more recently modifications are being explored for ENMs. These tests and the results they provide are distinct from those used for classifying explosive substances. Further, there are no criteria in the ADG Code (NTC 2007) or the GHS (2009) that allow classification of “explosive dusts” irrespective of whether the dust contains microfine materials or ENMs. These dusts are not classified as explosives (Class 1).

A comprehensive literature review by Eckhoff (2003) describes the physics of dust explosions and the development of test methods to predict dangerous combinations of materials and atmospheres. The focus of early studies was the investigation of the hazards of fine clouds of coal dust, wood, flour, common plastics (e.g. polyethylene powder) and reactive metals such as aluminium, magnesium and iron with a particle size between 10 and 150μm. The general findings for particles of this size and their concentrations in air are discussed in detail in Sections 3.4 to 3.6. For these microfine materials the data indicates the likelihood and severity of explosion increases with finer sized particles. However, at least for some explosive parameters there is an apparent particle size below which the trend for greater effect was restricted.

Research papers have focussed on evaluating the applicability of existing test methods and their modification, and validity of extrapolating the parameters describing the behaviour of microfine dusts to nano-sized particles. There are still many unknowns about the explosion hazard of nanomaterials.

One of the uses of nano-sized metal powders is in combustion systems. The high specific surface area of nano-sized metals (e.g. nano-aluminium) imparts high reactivity and short reaction times and have been shown to lower ignition temperatures compared to microfine particles (Risha et al. 2007). Kwok et al. (2002) investigated the thermal behaviour of two different aluminium (Al) nanopowders (mean particle sizes 12 and 90 nm) and a micro-sized Al powder (180nm) used as explosive propellants and in pyrotechnic compositions. The authors report significant differences in the way the nanomaterials behave; these include a lower onset of melting temperature (400-500^{o}C vs. 550-660^{o}C) and a higher reactivity in air. The authors suggested this was due to:

- The increased surface area of the nanopowder.
- The different thickness of the oxide layer which may be due to differences in aging and weathering. The oxide layer affected the reactivity of the Al powders and although it is not clear how the oxide films affect explosivity, their presence results in measurement of lower explosion characteristics (HSE 2004).
- Nano-Al was found to have higher electrostatic discharge sensitivities when compared to their microfine material counterparts. However, based on the data presented in this section on electrostatic ignition energy and dust explosivity, the dust explosion potential of both nano and micron sized Al powders would be classified in the most violently reactive class[6] (St 3) resulting in the same cautionary requirements in the handling of the powders.

3.2 Explosion Kinetics

Nanomaterials may present a safety hazard due to explosion hazards based on their physical properties (Dobashi 2009). In order to evaluate the probability of dust explosion and the degree of consequential damage an understanding of the ignitability and explosion violence (i.e. the explosion kinetics) is essential. In an industry setting such as a processing plant the dust may be present as a layer on surfaces or a cloud. Layers may produce an ignitable mixture when heated

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[6] St 3 is the highest designation used to classify combustible dusts as exhibiting very strong explosions. This designation is assigned based on the measured amount of deflagration observed in test data (i.e. the deflagration index, section 3.6).

or disturbed. According to Pratt (2000) "*in order to have an electronic ignition*" one of the requirements is that there is "*an ignitable mixture*". For this mixture to ignite there must be an energetic event that initiates an exothermic chemical reaction. Dusts dispersed in air are able to form such a mixture and ignite, and the ensuing combustion reaction may be violent enough to consider the dust cloud an explosive mixture. This is deflagration, i.e. propagation of combustion through air, as distinct from an explosive that mixes a fuel with an oxidiser to form an explosion, and this is why dusts are not considered for classification as Class 1 explosives.

The explosion kinetics, or the process leading up to a dust explosion, for a dust cloud is summarised in Figure 3.1. It shows the relationship of key parameters relevant to dust explosions. Once the concentration of particles in a dust cloud reaches the Minimum Explosive Concentration (MEC) in the presence of an ignition source above the Minimum Ignition Energy (MIE) then a dust explosion (deflagration) may ensue. The severity of this explosion is represented by the Maximum Rate of Pressure Change (R_{max}) that occurs after ignition. Hence the key parameters of explosion kinetics for a dust cloud are MEC, MIE and R_{max}. As discussed below these parameters are influenced by the dust particle size. They can be used to identify whether ignition and propagation of a flame will occur and to determine when a dust cloud may be in its explosive range.

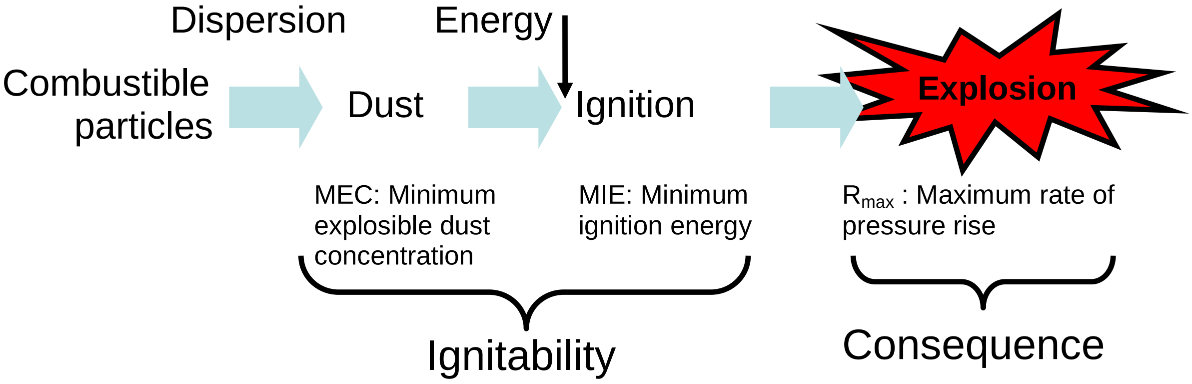

Figure 3.1: The explosion kinetics of a dust cloud (adapted from Dobashi 2009)

3.3 Testing key explosive severity parameters

Various apparatus have been used to measure parameters associated with explosivity of dusts (Pratt 2000). The Hartmann apparatus is most commonly used, a powder is suspended (in an enclosed explosion chamber of 20L) using pressurised air in the presence of an ignition source. Test chamber conditions are altered to determine the key parameters such as MIE and MEC. To identify the MEC the test is commonly performed at three to five concentrations between 500 and 2,500 mg/m^3 (OSHA 2008). The Maximum Rate of Pressure Change (R_{max}) during the explosion is also measured.

Modified Hartmann apparatus have been developed to account for limited sample availability of ENMs. Test aspects that have been explored include the use of different igniters, dispersion nozzles, construction materials and chamber sizes ranging from 1 to 20L, and through to large scale industrial equipment. These variations complicate comparison of data for nanomaterials with microfine material dusts.

Standard test methods, e.g. European Standards EN 14034-1(2004) and EN 14034-2 (2006), for determining key parameters of explosion severity require modification for evaluating nanopowders due to the lower amount of test material that is generally available. In these standards kilograms of microfine material are typically required per test. These standards refer to the explosion indices above, but also include the deflagration index (Kst), which is used to classify the dust explosion hazards (see Table 3.2). In an investigation commissioned by the UK Health and Safety Executive (HSE) modifications to test apparatus that allowed the use of smaller volumes of samples were trialled. However in these trials of ENMs there was often quenching of the flames. To account for differences due to quenching, a scaling factor obtained from the test data was introduced to calculate microfine equivalent scaled Kst values[7] (HSE 2010). Baseline measurements using previously characterised explosive materials were also performed to ensure values generated in the modified equipment were comparable (HSE 2010).

HSE (2010) also found the test equipment needed to be modified to overcome the non-homogeneous nature of nanomaterial-dust clouds. Agglomeration of nanoparticles may occur quickly and before combustion has been completed leading to localised rather than uniform ignition and pressure changes. The inhomogeneous nature of dust clouds further complicates interpretation of results (HSE 2010). As a result the modifications made to test apparatus have led to further complications regarding selection and interpretation of the criterion used to determine explosivity, for instance, whether propagation of a flame has occurred.

It is noted however that in real life situations, nanomaterial-dust clouds are likely to be non-homogenous and hence may not have the same characteristics as the experimental

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[7] Kst value is a dust specific explosivity characteristic determined from the maximum rate of pressure rise recorded after a combustible dust has been ignited.

nanomaterial-dust cloud in the test apparatus. Modifying test apparatus to obtain a ‘purer’ nano-cloud is presumably creating a worst case situation for the purposes of classification. This is a worst case because it is assumed a well dispersed dust cloud of nanoparticles is potentially more explosive than one with agglomerates of nanoparticles.

3.4 Minimum Explosive (Dust) Concentration.

The Minimum Explosive Concentration (MEC) is the lower limit of dust concentrations capable of resulting in an explosion.

The MEC is defined as the lowest concentration of dispersed dust that when ignited ruptures a paper membrane with a bursting strength of 0.2 bar[8] (Eckhoff 2003). Ensuring dust cloud concentrations in the workplace do not exceed MEC should reduce the possibility of dust explosions. It is apparent that measuring the key parameters of explosion severity including MEC is influenced by differences in apparatus used and the heterogeneity of dust clouds (Markis and Lee 1988).

This review has compiled MEC data from various sources for a range of different materials. Figure 3.2 shows the influence of particle size[9] on the MEC. Information from Eckhoff (2003), based on data sourced from Hertzberg and Cashdollar (1987), for coal and polyethylene has been reproduced in Figure 3.2. The limiting particle size[10] below which the MEC does not reduce further is approximately 10 - 100µm depending on the material, that is, there is a critical particle size determining MEC that is material dependent. The MEC is not dependent on particle size in the nano-range. Further increased particle surface area due to smaller particle sizes results in devolatilisation which is so fast that the combustion is controlled by gas mixing and gas combustion only (Echoff 2003) and MEC is not lowered below this limiting particle size.

The concept of a limiting particle size is supported by results published by others. The phenomenon has been demonstrated for various carbon blacks (Bouillard 2009), carbon nanotubes (Bouillard 2009, Vignes 2009) and aluminium (Wu 2010a, Mark 2004) (Figure 3.2).

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[8] This is an arbitrary pressure criterion introduced when the test was first developed in 1944 (Eckhoff 2003).

[9] Unless explicitly stated the particle size refers to the primary particle of a powder and not agglomerates that may be formed.

[10] The limiting particle size is the size below which no further change in the physicochemical property discussed is expected.

An important consideration according to Eckhoff (2003) is that the limiting particle size at the minimum explosive dust concentration is not necessarily the same as at higher concentrations, where the explosions are more violent.

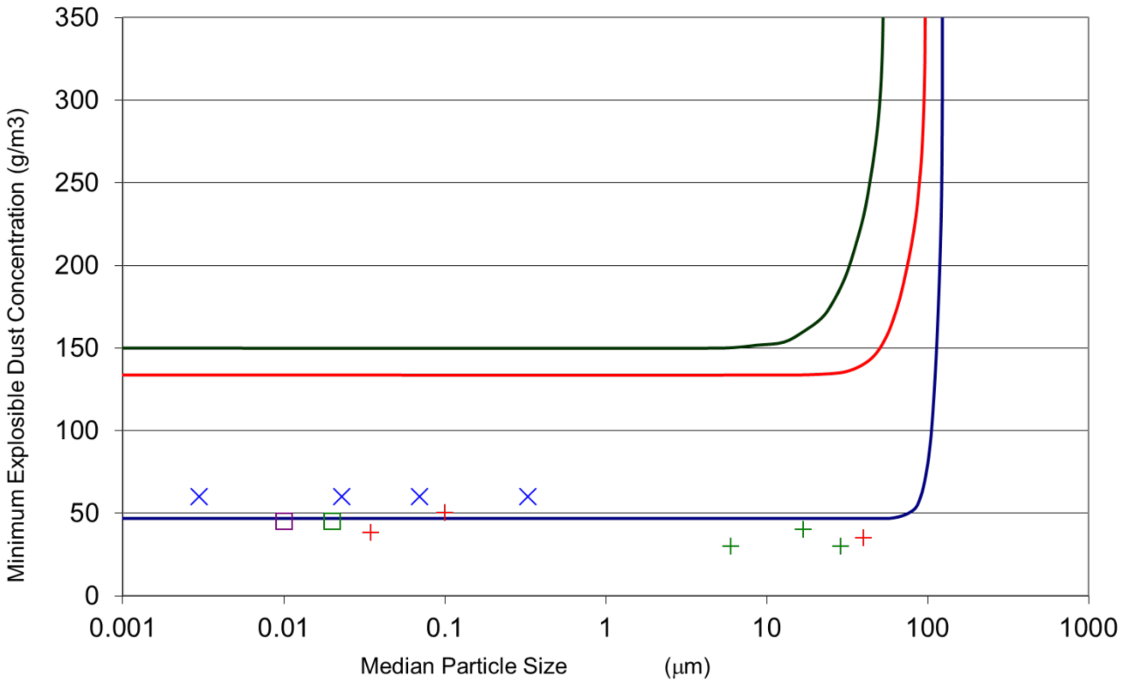

Figure 3.2: The Minimum Explosive Concentration (MEC) recorded for various micron-sized particles and nanoparticles (semi-log scale).

<u>Summary of MEC test data:</u> For any given material there appears to be a threshold for the minimum amount of dust in air required for explosivity. There is also a particle size threshold that is in the micron range, below which MEC does not decrease (i.e. the mass of dust in air required for an explosion does not decrease because the material may be nano-sized). The threshold differs for different types of material, however on face value the data imply reduction of particle size down into the nanometre range does not significantly influence this measure of explosivity.

With regard to the magnitude of the MEC, which appears to be between 30 and 70g/m^3 depending on the material, it should be noted that it is very large relative to the amount of airborne levels of

ENMs that have been measured in the workplace. Levels of ENMs in the workplace were reported to be less than 100μg/m^3 in a review of health hazards associated with use of ENMs (Table 4.1 in Safe Work Australia 2009). Further, the amount of material that is required to be present in a surface layer that may be disturbed to produce a dust cloud of ENMs that exceeded the MEC would be large. It is unlikely that the minimum MEC of 30g/m^3 would be reached in a well-managed work environment as a result of fugitive emissions from processes that involve nanotechnology processes. However, in the situations where production processes are not designed and/or controlled effectively (e.g. grinding of materials) or in handling processes there is potential for air concentrations in localised area to result in explosion.

3.5 Ignition sensitivity of dusts:

The Minimum Ignition Energy (MIE) is the minimum energy required to ignite a dust. The MIE is used as a measure of the ignition sensitivity of dusts, which is how easily the dust cloud will ignite. According to Pratt (2000) the minimum ignition energy of a combustible substance is the lowest electrical energy stored in a capacitor which, when discharged, will ignite the material at the conditions of the test.

Thus the MIE is a measure of the ignition characteristics of a mixture or substance, present as a gas or dust, and is used to identify reactivity. The MIE is an essential parameter in determining whether a dust can be ignited and lead to an explosion. The MIE is often used as a guideline for determining engineering protective measures required to minimise risk of ignitions by static electricity.

For dusts there are a number of material properties and test conditions[11] that affect the measurement and value determination of MIE (Pratt 2000). Hunt et al. (2008) showed that microfine aluminium particles (10 µm with a 4nm thick alumina passivated spherical shell) consistently required higher ignition energy than their nano-scale counterparts (18 and 50 nm with a 2 nm thick alumina passivated spherical shell). Thus nano-Al was considered more sensitive to ignition.

The MIEs reported from various studies for a range of micron-sized and nano-sized particles have been compiled and plotted in Figure 3.3. The figure is divided into three regions: very sensitive

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[11] Material properties and test conditions that affect measurement of MIE include particle size, particle concentration, particle shape, turbulence, ignition delay time, moisture content, electrode shape, electrode spacing, circuit inductance, circuit resistance, supporting atmosphere, temperature and pressure.

(MIE of <10mJ), sensitive (MIE of 10-1000mJ) and not sensitive (MIE >1000mJ) to ignition[12]. The MIE for polyethylene and aluminium were presented in a figure produced by Eckhoff (2003) that has been reproduced in Figure 3.3. The MIE data presented by Eckhoff (2003) was sourced from Pratt (2000) who noted that reducing the mean particle size from 500µm to 10µm reduced the MIE by two orders of magnitude. Eckhoff (2003) also showed similar trends for polyethylene, optical brightener and methyl cellulose and further noted that the reduction in MIE within this particle size range "*is very strong*", supporting the theory that MIE is proportional to the cube of the particle diameter (Kalkert 1979).

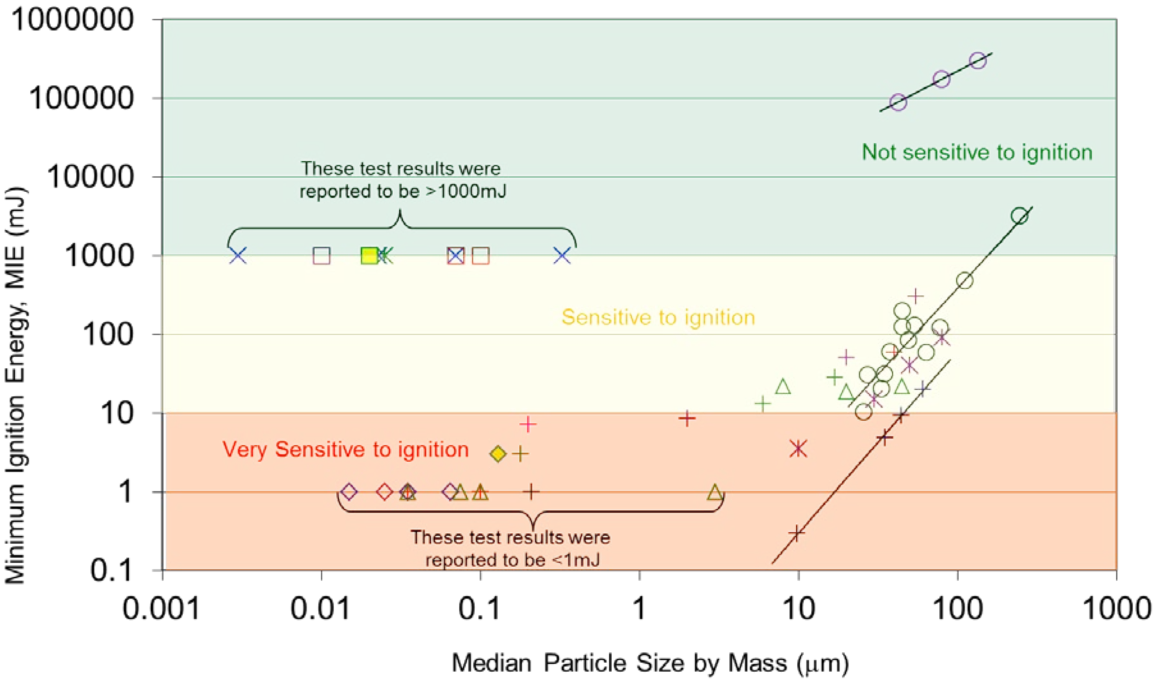
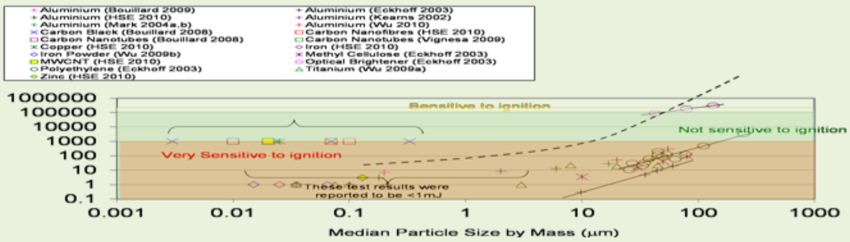


Figure 3.3: The Minimum Ignition Energy (MIE) recorded for various micron-sized and nano-sized particles (log-log scale).



Kalkert's (1979) theory is demonstrated by MIE data for polyethylene which shows a consistent fall in MIE over a large range of particle sizes (20-200µm). MIE data for aluminium powders from

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[12] To provide perspective, hydrocarbons in petroleum fuels have MIEs that range from 0.1 to 10mJ (Pratt 2000).

other studies (Kearns 2002, Mark 2004, Wu 2010a) are also provided in Figure 3.3; these data confirm the drop in MIE with decreased particle size for microfine particles. Assuming Kalkert's theory can be applied across a wide range of particle sizes, millimetre down to nanometre, MIEs would be expected to continue to decrease for nano-sized particles from the values obtained for their microfine material counterparts by a further two to three orders of magnitude. It is not clear from the data presented in Figure 3.3 whether the trend continues as the MIEs for particle sizes around 0.01 – 1 µm were at the limit of method reporting. The MIEs for aluminium reported by Bouillard (2009) are not decreasing with particle size as quickly as suggested. Although the MIE is decreasing with particle size it is uncertain whether the relationship between MIE and particle size observed in the micron range can be directly extrapolated to ENMs.

Nonetheless MIEs less than 1mJ signal the dust as being very sensitive to ignition and extreme caution is warranted when handling these materials (HSE 2010). One author suggests that more precise apparatus is required to assess the minimum ignition energy (<1 mJ) for susceptibility of nanomaterials. However unless another hazard category for this parameter is to be developed (e.g. 'extremely sensitive to ignition') there appears to be little point in determining the actual minimum ignition energy below 1 mJ since such materials are already categorised in the most sensitive category available for the parameter. Whether such a category would result in different management options over and above those associated with the current most sensitive category perhaps should be evaluated.

It is patent that airborne materials, that are easily ignited when in the microfine size range, may become more easily ignited (very low MIE) when present in the nano-size range. However a substance that is not easily ignited in the microform doesn't necessarily become so when nano-sized.

As observed with the MEC parameter, the MIE of a dust cloud, whether it be nano- or microfine-material, is dependent upon the nature of the material. The MIEs shown in Figure 3.3 for carbon nanotubes (Vignes 2009, Bouillard 2008), carbon nanofibres (HSE 2010), carbon black (Bouillard 2008) and multi-walled carbon nanotubes (MWCNT) (HSE 2010) are at least 3 orders of magnitude greater than the metallic nanoparticles (iron, titanium and aluminium) despite having comparable if not smaller particle sizes/diameters[13]. The MIEs are probably higher since they were reported as being greater than could be recorded by the experimental apparatus used by the investigators. These studies reveal the low ignition sensitivity of these dusts (Vignes 2009). The low ignitability of the carbon nanopowders relative to similar size metals was attributed to their

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[13] For nanofibres and tubes the diameter was taken to be the particle size. Where a range of diameters was listed and no average available, the minimum diameter was taken to be the particle size.

agglomeration (HSE 2010). Although carbon nanopowders were dispersed into individual nanoparticles for testing they quickly re-agglomerated. Agglomeration decreases the surface area available for taking part in ignition and flame propagation and therefore raises the MIE from that for well dispersed individual nanoparticles. Additionally, agglomeration of fine particles may affect dispersion of a dust cloud (Kearns 2004).

> <u>*Summary of MIE test data:*</u> *The available data is limited for MIE. Nano-sizing a microfine material is not sufficient in itself to indicate a dust cloud of the nano-material will become more sensitive to ignition. This is evident by a range of carbon compounds and iron as nanoparticles which remained as sensitive to ignition as the bulk microfine material. It is nonetheless clear that dust clouds of ENMs may be very sensitive to ignition when the larger micron scaled particle sizes are also sensitive. In other words, a microfine material that is easy to ignite when changed to be nano-size becomes more sensitive to ignition, but if it is not easy to ignite the microfine material, the nano-sized material may also not be easy to ignite.*
>
> *Under the current criteria for classifying sensitivity to ignition it is a moot point to pursue the relationship between MIE and particle size. At the current minimum level for measuring MIE, the highest sensitivity rating for ignition is reached and therefore improving ability to measure lower MIEs will not alter the current classification.*

3.6 Maximum rate of pressure rise

The maximum rate of pressure rise (R_{max}) is an index of the degree of explosion violence.

R_{max}[14] is measured alongside the MEC and has the same methodological drawbacks as previously discussed for MEC. The influence of particle size[15] on R_{max} is illustrated in Figure 3.4. R_{max} values for protein, starch, maize and aluminium provided in Eckhoff (2003) are well correlated with particle size in the range from 3 to 100µm, i.e. R_{max} increases as particle size decreases (as signified by the black dashed line in the micron particle size range on the right side of Figure 3.4). This correlation is supported by the data of Mark (2004) for microfine aluminium. This correlation however is not apparent for nanoscaled carbon nanotubes (Bouillard 2009),

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[14] R_{max} can be represented as $(\Delta p/\Delta t)_{max}$.

[15] Unless explicitly stated the particle size refers to the primary particle of a powder and not agglomerates that may be formed.

carbon nanofibres (HSE 2010), carbon blacks (Bouillard 2009, Vignes 2009) and MWCNT (HSE 2010). Data for nano-sized aluminium (Bouillard 2009, HSE 2010, Mark 2004a,b, Wu 2010a) also indicates that the particle size trend observed for microfine materials may not continue for ENMs; it may be argued that the reverse is true, i.e. that below approximately 0.3µm, R_{max} markedly decreases with decreased particle size (as signified by the black dashed line in the nano particle size range on the left side of Figure 3.4). However this observation should be considered with caution as a like for like comparison could not be performed, e.g. the data included different types of powders that was collected by different researchers using non-standardised equipment (Section 3.3).

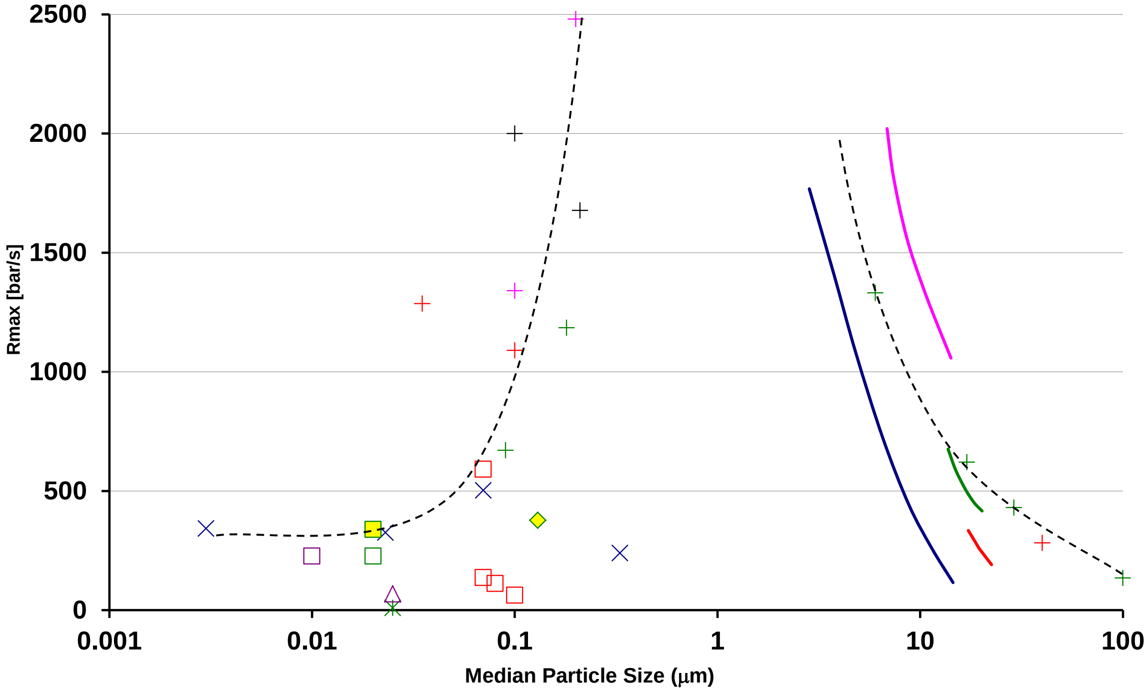

Figure 3.4: The Maximum Rate of Pressure Rise (R_{max}) recorded for various micron and nano-sized particles.

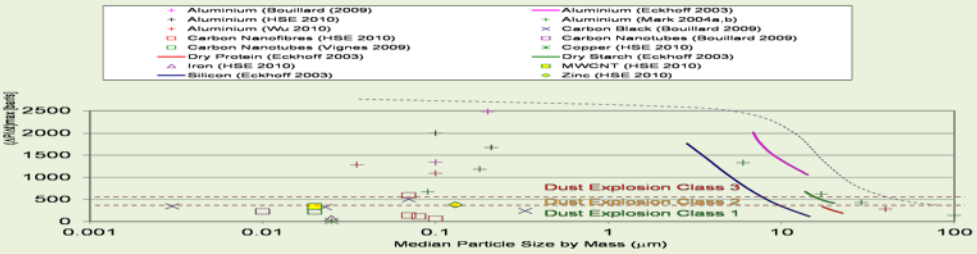

Figure 3.4 suggests the turning point at which the relationship between increasing explosion violence with decreased particle size reverses is between 0.3 – 3 µm. However more data is required within this size range and for more materials before a firm conclusion can be reached.

It is possible that the drop in R_{max} with decreasing particle size for ENMs, as indicated in Figure 3.4 by the black dashed line, is a result of quenching effects on the flame that is a reflection of the sheer number of ENMs particles present in the dust cloud. The result of this quenching means that although ENMs may be more easily ignitable than their microscale counterparts the consequences of the resulting explosion, i.e. the severity of the explosion, is potentially less for particles with diameters less than 0.1μm (or 100nm). It is important to note that this is a tentative interpretation of the available data that requires confirmation.

> *<u>Summation of R_{max} test data:</u> Although the test data for R_{max} is not complete there are three observations that can be drawn from the data available:*
>
> - *For a range of different materials there is a sharp increase in R_{max} values as particle size falls from 100 to 3μm.*
> - *There is a lack of data for particle sizes in the range of 0.3 to 3μm where there is potential for the highest R_{max} values to be recorded.*
> - *There is potentially a sharp decrease in R_{max} values, tentatively ascribed as a quenching effect, as particle size falls below 0.3μm into the nano-size range. This observation should be treated with caution.*

3.7 Classing dust explosions.

The deflagration index (Kst, bar.m/s) is used by some agencies to classify explosive dusts (OSHA 2008, HSE 2010). This is a constant that relates R_{max} to the volume occupied by the dust cloud (i.e. the volume of a test apparatus). However Kst cannot be considered a finite value intrinsic to the dust material as it is not only dependant on the volume, but also the geometry of the test apparatus. As test apparatus are being altered to suit testing of ENMs it may not be apparent how Kst is affected by nano-sizing materials unless tests are properly validated by comparison with data obtained from previous unmodified equipment.

Kst is calculated using equation 1 below:

$$K_{st} = R_{\max} \times V^{\frac{1}{3}} \qquad \text{---------------------------- Equation 1}$$

Where V is the internal volume (L) of the test chamber used to determine R_{max} (bar/s).

Kst is used to classify the explosion class of a dust using the criteria shown in Table 3.1 (OSHA 2008). It helps identify overpressures to which industrial equipment may be subjected. The information may be used so that in the event of a dust explosion destructive consequences are ameliorated through the use of techniques to vent, suppress or isolate rapid pressure build-up.

Table 3.1: The dust explosion class based on Kst-value (OSHA 2008)

Kst-value (bar.m/s)	Dust Explosion Class	Definition
Not ignitable	St0	No explosion
0 <Kst ≤200	St1	Weak explosion
200 <Kst ≤ 300	St2	Strong explosion
Kst> 300	St3	Very strong explosion

Kst is strongly dependent on the type of nanopowder. The Kst values for most aluminium nanopowders are above 300bar.m/s therefore they would fall into dust explosion class St3 (very strong explosion). However other metal nanopowders, e.g. zinc, iron and copper, have lower Kst values (<200bar.m/s) and therefore would into dust explosion class St1 (weak explosion).Although different types of carbon nanoparticles have different Kst values those that have been tested to date are all classed as St1 (Table 3.2).

> *Summary of dust explosion class values: The deflagration index (Kst) is used to classify the potential severity of a dust explosion. However the value of Kst is not only dependent on the intrinsic qualities of the dust but also on how explosive characteristics (R_{max}) have been tested. There is insufficient information available at this time to determine the influence that nano-sizing of bulk dusts may have on this index.*
>
> *Nevertheless a number of the metal nanopowders resulted in very strong explosions and were classified in the highest dust explosion class. It is noted validation of data from apparatus modified for testing ENMs is required.*

3.8 Summary of explosive hazards associated with engineered nanomaterials:

There is limited empirical data for ENMs with respect to the explosivity parameters MIE, MEC and/or R_{max}. A summary of the information is provided in Table 3.2. It is difficult to generate uniform dust clouds of ENMs that enables adequate testing, and techniques for measuring their explosivity parameters are evolving. Consequently it is not unexpected there are variations in the measured parameters. The limited data obtained with non-standardised methodology means there is uncertainty in the conclusions drawn from the available information.

Table 3.2: A summary of the key parameters involved in explosion kinetics of dust clouds for various nanoparticles.

Nano-material	**Source**	**MIE (mJ)**	**Ignition**	**MEC (g/m^3)**	**R_{max} (bar/s)**	**K_{st} (bar.m/s)**	**Explosive Class[a]**
Aluminium	Bouillard (2009), Eckhoff (2003), HSE (2010), Kearns (2002), Mark (2004a, b), Wu (2010).	<1 to 10	Very Sensitive	30 to 50	1000 to 2480	182 to 675	St2 or St3 (most St3)[b]
Iron	HSE (2010), Wu (2009b)	<1		nd	68	18	St1
Titanium	Wu (2009a)	<1		nd	nd	nd	n/a
Zinc	HSE (2010)	3-10		nd	377	101	St1
Carbon Black	Bouillard (2009)	>1000	Not Sensitive	50 to 70	240 to 503	65 to 136	St1
Carbon Nanofibres	HSE (2010)	>1000		nd	62 to 591	17 to 158	St1
Carbon Nanotubes	Bouillard (2009)	>1000		45	225	62	St1
Copper	HSE (2010)	>1000		nd	10	3	St1
MWCNT	HSE (2010)	>1000		nd	339	91	St1

nd = no data, n/a = not applicable

[a] Dust explosion classification according to Table 3.1.

[b] Different preparations of the same nanomaterial have different K_{st} values and therefore have different dust explosion classifications.

For an explosion hazard to be realised the concentration of ENM dust needs to be greater than its MEC and the energy of the ignition source needs to greater than the MIE for the substance. R_{max} and Kst are measures of the potential severity of an explosion should it occur. The following is a summary of these key properties for ENMs:

- *<u>MEC is independent of particle size for ENMs:</u>* The MEC reached a critical particle size in the μm range below which no further decreases in MEC were observed. A decrease in particle size into the nm range does not appear to affect this measure for ENMs. The available ENM data suggests a MEC threshold in the range of 3 0-70 g/m^3. This range is noted to be significantly higher than airborne ENMs measured in workplace air as a result of fugitive emissions from nanotechnology processes.

- *Some ENMs are very sensitive to ignition:* In the micron range decreasing particle size lowers the MIE. Unfortunately at sizes below 100nm the MIE reported for aluminium, titanium and iron ENMs were below the apparatus detection limit of 1mJ. Nevertheless they are considered to very sensitive to ignition since this MIE places them in the most sensitive category for ease of ignition. Copper and carbon nanoparticles had an MIE of >1000mJ hence these ENMs are not considered sensitive to ignition.

- *R_{max} increases with decreased particle size in the micron range however the opposite may potentially occur in the nano-size range:* The trend for ENMs is possibly due to flame quenching by increased particle numbers. R_{max} values are anticipated to reach their maximum levels in the 0.3 to 3μm particle size range but this requires additional data for confirmation.

- *The deflagration index (Kst) is used to classify the potential severity of dust explosions.* There is insufficient data to confidently judge the influence of nano-sizing materials on this index. Aluminium nanopowders have the potential for very strong explosions but not so for other nanometals despite being sensitive to ignition. Although carbon nanoparticles were not sensitive to ignition and had potentially weak explosions this does not necessarily rule out the possibility that the production of a dust cloud of carbon nanoparticles and subsequent exposure to an ignition source may not lead to a dust explosion.

A comparison of MEC, MIE and R_{max} data indicates that explosion severity of dust clouds filled with ENMs may not be proportionally worse than explosions from dust clouds filled with microfine materials. For ENMs the severity of explosion appears to be reduced with a decrease in particle size. However the MIE data suggests dust clouds filled with ENMs are more sensitive to ignition than microfine materials that are sensitive to ignition, and that these clouds have the potential to result in very strong explosions.

Predictions regarding the explosive potential of ENMs are uncertain for a number of reasons. Firstly there is limited data to compare with their micron size counterparts. Secondly, the comparisons performed in this review utilise test results from a variety of sources that used modified test equipment to overcome ENM testing difficulties. Hence the data are not strictly comparable.

The explosive hazard of ENMs should be assessed on a case by case basis preferably using standardised and validated test methods. In the absence of data it would be prudent to assume dust clouds from ENMs present an explosion hazard if the MEC is exceeded.

4. Known ENM related accidents

Summary of Dust Explosion at Gullaug, Norway 1973 (Eckhoff 2003).

An explosion in 1973 originated in the premix plant of a slurry explosive factory in Norway (Eckhoff 2003). The explosion occurred when loading a 5.2 m^3 batch mixer with 200 kg of very fine aluminium flake (thickness = 0.1μm or 100 nm, corresponding to a specific surface area of about 7.5 m^2/g), sulphur, and other ingredients under nitrogen. The total charge was 1200 kg. Investigations found that the minimum electric spark ignition energy was in the order of 1 mJ.

The mixing vessel was cylindrical, consisting of a feed chute at the bottom, with the device for mixing a vertical rubber-lined screw. During operation, the concentration of oxygen in the vessel was being controlled by a direct reading oxygen analyser. Investigation found the nitrogen (N_2) inerting system in the mixing vessel was inadequate. Both the N_2 inlet and the O_2 concentration measurement probe were located in the upper part of the vessel thereby making the measured O_2 concentration unreliable as an indicator for the O_2 concentration in the rest of the mixer. It is thought that the ignition source for the primary explosion was probably a propagating brush discharge[16], i.e. a high discharge energy that can initiate dust explosions.

The explosion resulted in five deaths, two seriously injured personnel, and two personnel suffering minor injuries. Given the presence of sulphur in the mixture, the accident cannot be confidently ascribed solely to the nano-nature of the aluminium flakes.

Mechanical attrition milling in Taiwan (Wu et al. 2009, 2010a, b)

Wu et al. (2010a) reported accidental explosions during the production of metal nanopowder by mechanical attrition milling. It is unknown whether this technique is used in Australia. Although Wu et al. (2010a) do not provide a case study they report accidents have occurred that are related to milling of aluminium from micro to nano-scale. The paper provides the explosion characteristics (maximum explosion pressure, maximum rate of pressure rise, minimum explosion concentration and minimum ignition energy) of aluminium powder and concludes the smaller the particle size,

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[16] Propagating brush discharges as a result of build-up of charges with opposite polarity in thin non-conductive layers (such as a dust layer, <8mm) results in high discharge energies (Eckhoff 2003).

the smaller the minimum ignition energy, with dust explosion presenting a serious threat when aluminium material is milled down to nanoscale.

A related paper by the same research group (Wu et al. 2009) implies all of Taiwan's nanoscale-powder manufacturing units have at one time experienced a dust explosion. The paper provides data for the MIE of nanoscale titanium and iron showing that the energy requirements for the nanoscale powders are less than micron scale powders, and more importantly less than the energy considered to be generated from impact, friction and/or grinding sparks (Wu et al. 2009, Siwek and Cesena 1995).

Wu et al (2010b) report an explosion which occurred in a steel factory in Taiwan in which microscale iron dust was carried at high pressure (12.5 kg/cm^2) in oxygen. The impact of the high pressure dust on pipe bends resulted in an explosion which destroyed the pipes causing 1 fatality and 7 injuries. Wu et al. (2010b) indicate an analysis of the incident was used to simulate the conditions for a high pressure gas carrying nanoscale aluminium, titanium and iron. The study found that explosions could readily occur for titanium powder at all air flows, and iron powder at oxygen flows greater than 3.5 m/s. Aluminium powder exhibited no explosion or sintering at all flow rates. Similarly when pure nitrogen was used as a carrier gas, no explosions occurred for all three types of nanograde metal powders. The minimum ignition energies of all metal nanopowders were <1 mJ. Wu et al (2010b) concluded a more precise minimum ignition energy detection (i.e. < 1mJ) instrument is required to assess the susceptibility of dusts to explosions.

5. Safety hazards in the nanotechnology workplace

Currently in Australia there are over 75 research organisations and 80 nanotechnology companies involved in researching or developing nanotechnology (DIISRTE 2011). It has been estimated the workforce involved in research is more than 2,500 people. The number of workers in a typical occupational setting using ENMs may be potentially much larger. To understand whether workers are suitably informed regarding the safety (physicochemical) hazards associated with the use of ENM the following questions have been considered:

- Is current information supplied with ENMs (i.e. SDS) suitable to allow workers to understand the safety hazards presented by ENMs?
- Where information on the physicochemical properties supplied is insufficient, what capability exists for testing the ENM?
- What are the implications for the protection of worker safety?

5.1 Review of information supplied with ENMs

Safe Work Australia (2010) has previously published a review of the information provided in SDS for ENMs that identified limitations in the relevant health and safety information provided. Only 16% of the SDS reviewed provided a description of the health and safety information that was considered “adequate and accurate” to inform an occupational risk assessment (Safe Work Australia 2010). The review performed by Safe Work Australia (2010) also found:

- Specific descriptions and data for the ENM was not provided in many of the SDS reviewed.
    - In contrast, the accompanying technical literature typically described physicochemical properties pertaining to nanometrology (i.e. particle size, surface area, pore size and volume, particle size and shape, dispersibility etc.).
- Suggested control measures were general statements that applied to bulk materials with larger particle size.
- Only 13% of SDS contained specific recommendations for extraction (local exhaust ventilation).
- The description of the chemical and physical properties was also found to be insufficient in previous surveys of SDS performed by other organisations.

The Safe Work Australia (2010) review collated information on the hazard classification in the SDSs. The majority of ENMs were identified as hazardous substances in the SDS, however only a small proportion were identified as dangerous goods (See Table 5.1 below). Carbon nanotubes and silicon compounds were classified as non-dangerous goods. Half of the ENM metal powders (including oxides) were classed as dangerous goods however a number of them were dispersed in a medium that contained a solvent that was itself classed as a dangerous good. This may have driven the classification rather than the properties of the ENM. A large proportion (53%, 9/17) of the metal ENM were powders, with 33% (3/9) classed as flammable solids. A warning of associated explosion hazard as a result of the generation of combustible dusts was provided only for the flammable solids (3/34). None of the SDSs provided explosive limits and none provided a warning of associated explosion hazards for ENMs as a result of the generation of combustible dusts. It is concluded from this evaluation that current SDSs for ENMs do not provide adequate physicochemical data or safety information.

Table 5.1: Hazardous and Dangerous Goods information provided in select SDS for available ENMs.

Type of Engineered Nanomaterial	**Carbon Nanotubes**	**Metal ENM** [a]	**Silicon Compounds**
Number of SDS revisited [b]	11	17	7
Classified as hazardous.	100%	76%	71%
Provided an adequate and accurate description of hazard.	0%	47%	0%
Classified as Dangerous Goods.	0%	53%	0%
Provided physicochemical properties.	20%	18%	0%
Provided explosive limits or ignition temperature.	0%	0%	0%
Warning of Dust explosion.	0%	18%	0%

[a] 9 of the 17 SDS were metal powders (including oxides). The remaining metal powders were dispersed in a solvent or other medium.

[b] 34 of 49 SDS assessed in the Safe Work Australia (2010) review were revisited for assessing information provided in this table. The remaining ENM (classed as ‘other’ in the review) were dispersed in a paste and not considered further.

Safe Work Australia published the model Code of Practice on *Preparation of Safety Data Sheets for Hazardous Chemicals* in December 2011 (Safe Work Australia 2011). Under WHS regulations, SDS must be provided for chemicals that are classified as hazardous. However many nanomaterials are not currently classified and thus if the bulk form is not classified as hazardous, SDS may not be provided for ENMs. To address this situation, the SDS code notes that ‘For engineered or manufactured nanomaterials or chemicals containing engineered or manufactured nanomaterials, an SDS should be provided unless there is evidence that the nanomaterials are not hazardous.’

For the purpose of evaluating the hazards associated with the generation of combustible dusts in general, a description of physicochemical data would be useful, such as:

- Nanometrology (i.e. particle size, surface area, pore size and volume, particle size and shape, dispersibility etc).
- Combustibility/Explosivity parameters (i.e. MIE, MEC, R_{max}, Kst).
- Dustiness. Although not discussed previously this parameter may provide useful insight into the likelihood that a dust cloud is generated.
- Self-ignition temperature.
- Incompatible substances.

Some of the physicochemical properties listed above appear in Section 9 of the SDS code. However it is recognised that many employers and workers may not be able to interpret data listed above. It would be provided primarily for professional engineers and those competent in the nuances of classification of explosives. The practical information required by workers is whether a dust explosion hazard exists when handling the ENM, and how this may be mitigated by appropriate work practice. It would also be useful to include information on practices that increase the explosive hazard.

For SDS it is apparent that there is not a suitable dangerous goods classification for the hazards associated with dust clouds (i.e. likelihood and severity of explosion). The classification would be beneficial for both ENMs and microfine materials alike. This issue is being considered by a correspondence group formed by the UN Sub-committee of Experts on GHS (SCEGHS) to collect information on dust explosion hazards (GHS 2012), including:

- Existing definitions or criteria for dust explosion hazards including any analytical methods used and any methods for determining related relevant safety data;
- Requirements (if any) for hazard communication on labels and SDSs;
- Explosion protection concept and derived safety measures; and
- Identification of issues related to addressing dust explosion hazards in the GHS, if any.

The correspondence group has also considered various options on how to address dust explosion hazards in the GHS.

In addition, ISO has developed a Technical Report on *Preparation of safety data sheets (SDS) for manufactured nanomaterials*, which was published late in 2012. Use of the advice in this Technical Report should help manufacturers and importers to provide accurate and relevant information in SDS for nanomaterials.

5.2 Implications for the use of ENM in the workplace

There is limited information available to enable a person in control of a business, managers of a workplace and their workers to identify whether safety hazards such as explosivity are associated with ENMs. Issues that limit the workplace usefulness of currently available data for physical hazards of ENMs include:

- Research literature which is insufficient to predict pivotal cut-off values for ENMs (i.e. MIE, R_{max}, MEC) that could be used for categorising explosivity (see Chapter 3).
- Insufficient information to enable confident extrapolation of the physical hazards of bulk material to ENMs.

- Technical literature (i.e. SDS) that provides insufficient information for identifying and assessing ENM physicochemical hazards.

ENMs should be assessed on a case by case basis. Where possible the key physicochemical parameters should be determined by standardised and validated methodology for ENMs. This will allow the adoption of targeted workplace practices to minimise risk of harm. Where these key properties are not known, a precautionary approach should be adopted and workplace procedures implemented to reduce or remove the possibility of dust cloud formation. At this time it is not unreasonable to assume a default position that ENMs, because of their nano-size and accompanying increased reactivity, would potentially present a greater likelihood of explosion from generation of combustible dusts than corresponding bulk materials. The key implication for the workplace is that this may not be appreciated or identified either by the workforce or design engineers. Examples of the consequences of failing to identify the hazard have been described for two workplace related incidents that resulted in “accidental” explosions and death of workers (Section 4).

Notwithstanding the above there are standard measures currently used for dusty materials and chemicals that can be put in place to reduce the likelihood of explosion from ENMs. The measures provided here are not complete or exhaustive however they could easily apply to the use of ENMs as well as microfine materials and/or chemicals in the workplace. These mitigation strategies have been drawn from the European Strategy for Nanosafety series of documents (EU 2008a, EU 2008b, EU 2008c, EU 2008d, EU 2008e). The reader is directed to those documents for greater detail on the safe production and use of ENMs.

Workplace procedures to reduce the possibility of a dust explosion could include:

- The use of wet processes allowing staff to work with nanomaterials in an agglomerated state or dispersion.
- Working in well ventilated workspaces that provide efficient exhaust with particle filtration.
- Implementing good housekeeping to minimise the build-up of dust layers that may be disturbed to form dust clouds.
- A confined process. This may include incorporation of a protection barrier such as a venting system to reduce the severity of an incident or a prevention barrier to reduce probability of an incident.
- An inert process, i.e. a process that does not build an explosible dust/air mixture or a process that does not have ignition sources.

It may not be generally appreciated that ENMs tend to stay airborne for considerably longer periods of time when compared to their micron sized counterparts. Whereas micron-sized particles tend to settle out the ENMs are more likely to produce dust clouds with a steady dust concentration for relatively long periods of time. However for the dust explosion hazard to be realised the dust concentration must be at least equivalent to the MEC. It has been noted in Section 3 that the current information, albeit limited, suggests the MEC for ENMs is significantly greater than the airborne concentration measured in workplaces to date. While reassuring this does not address the possibility of air concentrations becoming higher in localised areas, e.g. very close to emission sources such as grinding processes and in ventilating equipment and ducts.

The prevention of dust accumulation in the workplace minimises the likelihood of dust cloud formation as a result of any sort of disturbance. According to HSE (2004) one of the noted ways in which a dust explosion can occur is by a small primary explosion that leads to a larger secondary explosion; i.e. the ignition of the dust cloud that may be formed.

5.3 Australian capability for testing ENM

There is support in Australia for the development of nanometrology infrastructure (NMI 2011), however the focus of these research activities is on dimensional measurements and dispersion state of ENMs. Research and development in physicochemical metrology is in its infancy and there are many important properties that require consideration. There is also limited consensus on the properties that should take precedence in requiring measurement.

Two Australian laboratories were identified that currently have the capabilities to measure physicochemical parameters of ENMs associated with combustibility and explosivity. Other laboratories were also identified that measured these parameters for micrometer sized particles, however they do not provide the service for ENMs due to the safety considerations and the validity of tests (agglomeration effects, sample size/availability etc.).

Further information on nanotechnology research facilities is available from the Australian Nanotechnology Network: http://www.ausnano.net/index.php?page=groups&group=145

Further information on performing explosive testing of dusts is available from Testsafe and/or Fire Protection Technologies:
http://www.testsafe.com.au/flammable_dusts.asp
http://www.fire-protection.com.au/ExplosionProtection/Testing.aspx

6. Conclusions

The evaluation of safety hazards associated with use of ENMs in the workplace is primarily focussed on their explosive potential when they form dust clouds. Little information was found for ENMs that related specifically to the other physiochemical hazards and hazard classifications as set out in the GHS (2009) and ADG Code (NTC 2007). The following is a summary of the key parameters relating to the explosion hazard (MEC, MIE and R_{max}) of ENMs:

- For ENMs the minimum explosive concentration (MEC) is independent of particle size. The concentration of ENM required in a dust cloud to exceed the minimum concentration needed for explosion is several orders of magnitude higher than airborne levels of ENMs that have been measured in the workplace as a result of process emissions, however there is potential for air concentrations in localised area to result in explosion, e.g. near a grinding process. In addition dusts of nano-materials stay airborne longer than dusts comprised of micron-sized particles.

- The minimum explosive energy (MIE) required to initiate a dust explosion indicates ENMs are potentially very sensitive to ignition when their microfine counterparts were also sensitive. However if a micro-size substance is not likely to be ignited then reducing the particle sizes down to the nano-scale does not necessarily mean it becomes sensitive to ignition.

- The potential severity (R_{max}) of an explosion increases with decreased particle size in the micron size range. However it appears this trend does not continue into the nanometre range. The available data indicates R_{max} may exhibit a sharp decrease in magnitude for ENMs when particale size decreases below approximately 0.3 μm. Therefore the severity of explosion for ENMs is potentially less than their microscale counterparts, even though they may be more easily ignited. Additional data is however required to confirm the discordant R_{max} observations for micro-size material and nano-size materials.

Together, these pivotal properties indicate the explosion severity of dust clouds filled with ENMs may not be proportionally worse than other dust clouds as might be anticipated by their relative increased surface area. It should be noted however that some ENM dust clouds are still able to result in very strong explosions.

As indicated the available physicochemical data for ENMs is directed towards explosivity of dust clouds. In the GHS (2009) and ADG Code (NTC 2007) there is no specific dangerous goods category to account for this hazard. A specific classification criterion for dust explosion would be beneficial.

Predictions regarding explosive potential of ENMs are uncertain for a number of reasons. Firstly there is limited data spanning the particle size range of interest and only relatively few ENMs have been investigated. Secondly, the comparisons with bulk materials performed in this review relied on test results that are not easily compared because they come from a variety of different sources. These research investigations used modified, non-standardised test equipment to overcome testing difficulties associated with ENMs that are not encountered with micro-fine dusts.

With regard to workplace implications, the dearth of data makes it difficult to draw general conclusions about the physicochemical safety aspects of ENMs that are related to their nano-size characteristic. It is nonetheless recognised the explosive behaviour of airborne ENMs is different to their microfine material counterparts; some may be more easily ignited but the explosion severity is not expected to be worse. It appears that the air concentrations of ENMs required for an explosion are much higher than what will be readily realised in a well-managed workplace however there is potential for air concentrations in localised areas (e.g. as a result of grinding process) to result in explosion.

Notwithstanding the above, it is prudent:

- for ENMs to be assessed for explosivity on a case by case basis, preferably using standardised, validated test methods.
- in the absence of specific information, to assume dust clouds of ENMs present an explosion hazard.
- for precautionary information regarding explosivity to be provided on safety data sheets irrespective of whether bulk chemical is classified as explosive.

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8. Useful links

Definitions may be obtained from the following sources:

- ISO (2008a). Nanotechnologies - terminology and definitions for nano-objects - nanoparticle, nanofibre and nanoplate. International Organization for Standardization.

- Nanotechology Now:
  http://www.nanotech-now.com/nanotechnology-glossary-A-C.htm

- Institute of Nanotechnology, UK:
  http://www.nano.org.uk/nano/glossary.htm

- Northwestern University:
  http://www.discovernano.northwestern.edu/whatis/Glossary

- U.S. National Cancer Institute:
  http://nano.cancer.gov/resource_center/nanotech_glossary.asp

- Nano forum (European Nanotechnology Gateway):
  http://www.nanoforum.org/nf06~struktur~0~modul~loadin~folder~143~.html

- Nanosafe:
  http://www.nanosafe.org/glossary

- Nanotech BC, Canada:
  http://www.nanotechbc.ca/main/resources_/1083/

9. Glossary of terms

Agglomerate: collection of weakly bound particles or aggregates or mixtures of the two where the resulting external surface area is similar to the sum of the surface areas of the individual components [ISO 2008a, ISO/TS 27687:2008(E) definition 3.2].

Aggregate: particle comprising strongly bonded or fused particles where the resulting external surface area may be significantly smaller than the sum of calculated surface areas of the individual components [(ISO 2008a, ISO/TS 27687:2008(E) definition 3.3].

Bulk material: For this report a bulk material is considered to be one with all dimensions above 1mm in size.

Corrosive to metals: A substance which by chemical action will materially damage, or even destroy, metals (ADG 2007).

Corrosivity: A property that relates to substances that are corrosive to metals.

Carbon nanotubes: Tiny tubes about 10,000 times thinner than a human hair -- consist of rolled up sheets of carbon hexagons (ASCC 2006). Abbreviation **CNT**.

Deflagration: the action of heating a substance until it burns away rapidly (Oxford online dictionary).

Engineered nanoparticles: A nanomaterial designed for a specific purpose or function. Abbreviation **ENM** (ISO 2010).

Explosive substance: An explosive substance (or mixture) is a solid or liquid substance (or mixture of substances) which is in itself capable by chemical reaction of producing gas at such a temperature and pressure and at such a speed as to cause damage to the surroundings (ADG 2007

Explosivity: A property that relates to explosive substances.

Flammability: A property that relates to flammable substances (e.g. flammable soilds).

Flammable solids; readily combustible solids and soilds that may cause fire through friction (ADG 2007)

Kst: The deflagration index determined from R_{max} and used to classify the explosion class of dusts.

MEC (Minimum explosive concentration): is the lowest concentration of dispersed dust that generates a pressure rise greater than 0.2 bar/s when ignited.

MIE (Minimum ignition energy): the minimum amount of energy required to ignite a dust cloud by an electrostatic discharge.

Microfine Materials: Materials with at least one dimension in the micron range (μm) and none smaller.

Multi-walled carbon nanotubes: Carbon nanotubes (q.v.) which consist of more than one nanotube completely contained within another (ASCC 2006).

MWCNTs: Abbreviation for multi-walled carbon nanotubes (ASCC 2006).

Nano: 10^{-9} [ISO 2008a, ISO/TS 27687:2008(E)] or, alternatively, 0.000000001 (ASCC 2006).

Nanometrology: The science of measuring characteristics of materials in the nanoscale.

Nanoaerosol: A collection of nanoparticles suspended in a gas (ASCC 2006).

Nanoengineering: The construction of nanostructures and their components (ASCC 2006).

Nanofibre: nano-object with two similar external dimensions in the nanoscale and the third dimension significantly larger [ISO 2008a, ISO/TS 27687:2008(E) definition 4.3]. Note that a nanofibre can be flexible or rigid, the two similar dimensions are considered to differ in size by less than three times and the significantly larger dimension is considered to differ from the other two by more than three times, and the largest dimension is not necessarily in the nanoscale.

Nanomanufacturing: Is expected to be high- volume, high- rate, integrated assembly of nano-elements into commercial products. This involves controlling position, orientation, and interconnectivity of the nano- elements (ASCC 2006).

Nanomaterials: Material with any external dimension in the nanoscale or having internal structure or surface structure in the nanoscale. Note: This generic term is inclusive of nano-object and nanostructured material (ISO 2010).

Nano-object: material with one, two or three external dimensions in the nanoscale [ISO 2008a, ISO/TS 27687:2008(E) definition 2.2].

Nanoparticle(s): nano-object with all three external dimensions in the nanoscale [ISO 2008a, ISO/TS 27687:2008(E) definition 4.1]. Note that if the lengths of the longest to the shortest axes of the nano-object differ significantly (typically by more than three times), the terms nanofibre or nanoplate are intended to be used instead of the term nanoparticle. Abbreviation: **NPs**.

Nanoplate: nano-object with one external dimension in the nanoscale and the two other external dimensions significantly larger [ISO 2008a, ISO/TS 27687:2008(E) definition 4.2].

Nanopowder: Dry nanoparticles (ASCC 2006).

Nanoscale: size range from approximately 1 nm to 100 nm [ISO 2008a, ISO/TS 27687:2008(E) definition 2.1].

Nanoscience: The study of phenomena and manipulation of materials at atomic, molecular and macromolecular scales, where properties differ significantly from those at a larger scale (ASCC 2006).

Nanostructures: Nanometre sized objects. Chemically, nanostructures are molecular assemblies of atoms numbering from 10^3 to 10^9 and of molecular weights of 10^4 to 10^{10} Daltons. Thus, they are chemically large supramolecules. To molecular biologists, nanostructures have the size of objects such as proteins or viruses and cellular organelles. Material scientists and electrical engineers view nanostructures as the current limit of nanofabrication (ASCC 2006).

Nanotoxicology: The study of the adverse effects of nanoparticles (NPs) on health and the environment (ASCC 2006).

Nanotubes: hollow nanofibre [ISO 2008a, ISO/TS 27687:2008(E) definition 4.4].

NPs: Abbreviation for engineered nanoparticles (q.v.), c.f. UFPs (q.v.) (ASCC 2006).

Particle: minute piece of matter with defined physical boundaries [ISO 2008a, ISO/TS 27687:2008(E)definition 3.1].

Particle size: Size of a particle as determined by a specified measurement method (ASCC 2006).

Permissible Exposure Limit (PEL): OSHA (USA) guideline/standard for maximum workplace exposure over an 8-hour time weighted average (TWA) exposure. Equivalent to Australian WES (Workplace Exposure Standard) (ASCC 2006).

Pyrophoric substances: a substance which, even in small quantities, is liable to ignite within five minutes after coming in to contact with air (ADG 2007). (Also see self-heating substances):

Pyrophoricity: A property that relates to pyrophoric substances (e.g. flammable soilds).

Quantum dots: crystalline nanoparticles that exhibit size-dependent properties due to quantum confinement effects on the electronic states [ISO 2008a, ISO/TS 27687:2008(E) definition 4.7].

R_{max}: The maximum rate of pressure rise recorded after a combustible dust has been ignited.

Self-Accelerating Decomposition Temperature (SADT): means the lowest temperature at which self-accelerating decomposition may occur without with substance as package (ADG 2007).

Self-heating substances: a substance or mixture other than a pyrophoric liquid or soild, which, by reaction with air and without energy supply, is liable to self-heat. This substance differs from a pyrophoric substance (ADG 2007).

Self-reactive substances: means a thermally unstable liquid or solid substance liable to undergo a strongly exothermic decomposition even without participation of oxygen (ADG 2007)

Single walled carbon nanotubes: Carbon nanotubes (q.v.) which do not contain any material internally (ASCC 2006).

Specific surface area: Ratio of the surface area to the mass of a nanopowder (ASCC 2006).

Specific surface area mean diameter: diameter calculated from a ratio of particle volume to specific surface area adsorption [ISO 2008a, ISO/TS 27687:2008(E) definition A3.1].
NB: applicable for non-porous spherical nanoparticles and often carried out by the BET method.

SWCNTs: Abbreviation for single-walled carbon nanotubes (ASCC 2006).

Ultrafine particles: particle with an equivalent diameter less than 100 nm (most nanoparticles, defined by their geometrical dimensions, are ultrafine particles, when measured) [ISO 2008a, ISO/TS 27687:2008(E) definition A3.2].

Workplace exposure standard (WES): Safe Work Australia guideline/standard for maximum workplace exposure over an 8-hour time weighted average (TWA) exposure. Equivalent to US PEL (Permissible Exposure Limit) (ASCC 2006).

Appendix 1: Literature Search Strategy

Literature Search Strategy: Evaluation of Potential (Physicochemical) Hazard Associated with the use of Engineered Nanomaterials

The main goal of this literature search was to find information regarding the safety hazards due to physical/chemical properties of engineered nanomaterials. An investigation was carried out at the start of the project to assess the most relevant search terms that would give the highest number of relevant results. The investigation was used to assess the success of particular search terms. During the literature search the following terms were used:

- “engineered nanoparticle(s),”
- “engineered (nanomaterials or nanoparticle) AND (research or method or properties).”
- Nanomaterial AND (safety or hazard) or Nanoparticle AND (safety or hazard)
- Engineered nanomaterial OR nanoparticle AND explosivity
- Engineered nanomaterial OR nanoparticle AND flammability
- Engineered nanomaterial OR nanoparticle AND catalysis
- Dust explosion AND nanomaterials or nanoparticle
- Nanomaterial or nanoparticle AND accident

Additional terms were used including author searches to refine particular research questions.

The following databases were included in the literature search strategy:

- CRC NETBASE
- ENGNETBASE
- NANOnetBASE
- MaterialsnetBASE
- ScienceDirect
- Informaworld
- Knovel library
- Wiley Interscience
- American Chemical Society Publications (ACS)

Because it was logistically impossible to read every single article, titles and abstracts were screened for relevance. For those that passed screening, full text articles were acquired. A list of subject matters serving as screening criteria for relevance are given below. The criteria is by no means limited to these few dot-points, but they nevertheless were used as a guide.

- Any mention of physicochemical properties
- Hazards associated with handling engineered nanomaterials (in the workplace)
- Safety tests or checks for workers handling engineered nanomaterials
- Uses of engineered nanomaterials (which may shed some light as to what safety hazards are associated with that specific undertaking)

Apart from the peer-reviewed literature from books and journals, the second aspect of the literature search looked at current working papers and reviews by competent authorities. The titles of the reviews tend to be very general, and content is not be limited to the research topic of interest. However, these reviews were screened for relevant parts. Competent authorities interrogated include:

- UN Expert Committee on Dangerous Goods
- Organisation for Economic Co-operation and Development (OECD)
- European Centre for Ecotoxicology and Toxicology of Chemicals (ECETOC)
- American Chemistry Council
- British Health and Safety Executive (HSE)
- German Federal Institute of Occupational Safety and Health (BAuA)
- The Council for Science and Technology
- UK Department for Environment, Food and Rural Affairs (DEFRA)
- European Commission (EC)
- Nordic Council
- United States Environmental Protection Agency (US EPA)
- Canadian Centre of Occupational Health and Safety (CCOHS)
- Google Search

The literature search includes information published up until November 2011.