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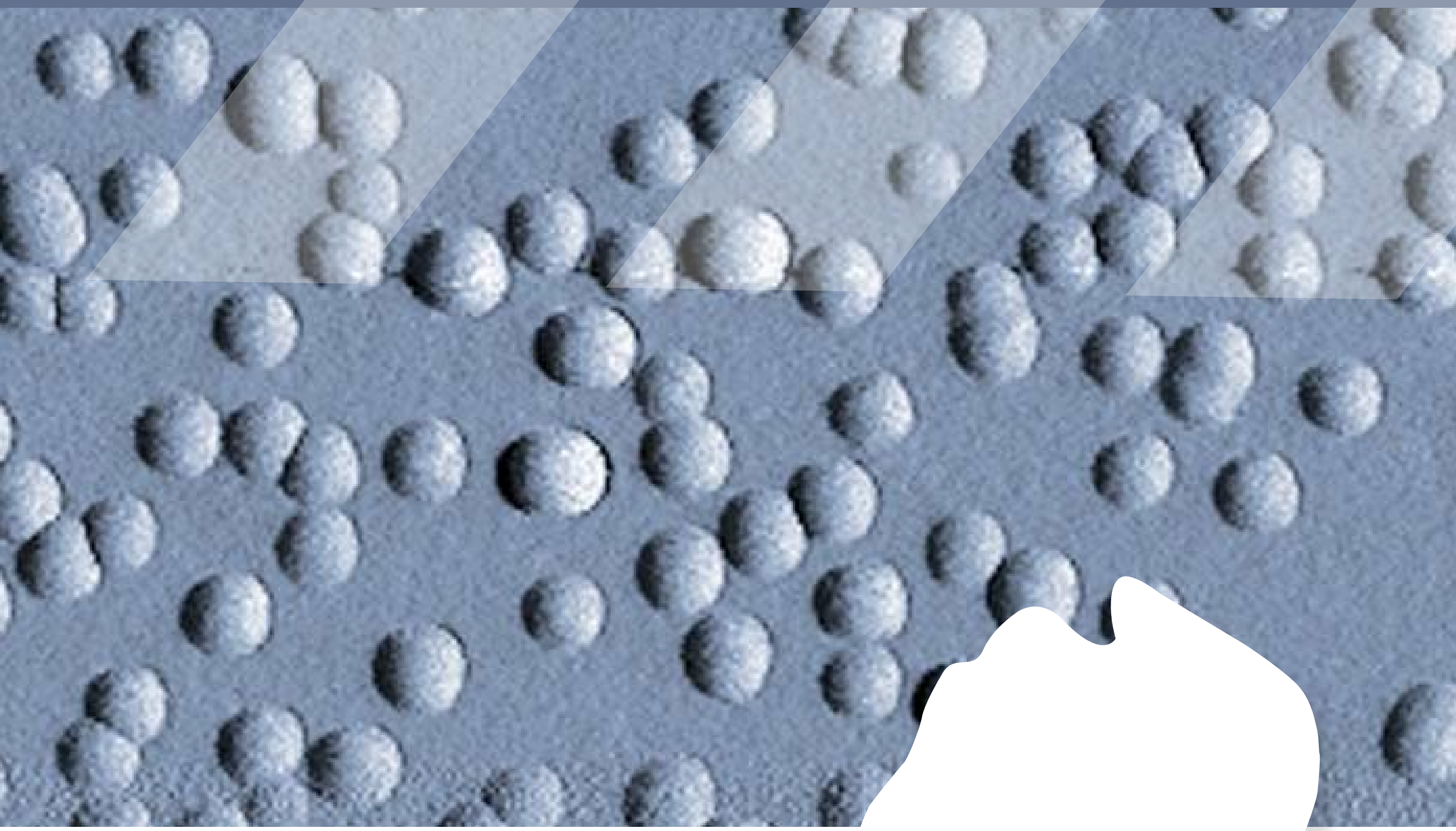
An Evaluation of MSDS and Labels associated with the use of Engineered Nanomaterials



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Executive Summary

This review reports an evaluation of 50 Material Safety Data Sheets (MSDS) and 15 labels for products containing Engineered Nanomaterials (ENM).[1] The evaluation considers how information on current ENM MSDS and labels reflects the state-of-knowledge in regard to the hazards, risks and controls. The report provides an assessment of the relevance, accuracy and context of the information presented on the evaluated MSDS & labels for the protection of health and safety in the workplace. In addition the evaluations consider how the ENM MSDS and labels comply[2] with the Australian National Codes of Practice for MSDS & Labelling [NOHSC:2011(2003)] and [NOHSC:2012(1994)] respectively.

MSDS

MSDS obtained were categorised in the following manner:

- Metals & metal oxides (17)
- Silicates (7)
- Carbon nanotubes (CNTs) (12)
- Other (14)

Most products were classified as hazardous (82%) and the most frequent classification for engineered nanomaterials (ENM) was as an irritant (R36/R37). Of those produced in Australia (36%), 89% conformed with the Australian Code of Practice for Preparation of MSDS [NOHSC 2011(2003)].

The date of preparation for most MSDS (79%) was less than five years ago (i.e. 2004 – 2009) and more than half of these (56%) were prepared during 2008 or 2009. Seven MSDS did not contain a date and three were produced from 2000-2003. [3]

Most of the MSDS evaluated (84%) did not provide adequate and accurate information sufficient to inform an occupational risk assessment for nanomaterial contained in the product.

Some of the major findings of the MSDS assessment include:

- Although all CNTs were classified as hazardous substances, eleven out of twelve MSDS described the hazards of CNTs to be equivalent to that of graphite (i.e. irritating to skin/eyes/respiratory tract). This assumption is not in line with currently available reviews and scientific studies on the health effects of CNTs. An Australian MSDS included the classification as "*R68/20 Harmful: possible risk of irreversible effects through inhalation (limited evidence*)". The risk phrase was accompanied by a cautionary note in Section 2 Hazard Identification.

[1] Section 1 details the search strategy for MSDS and labels.
[2] Only considered for MSDS and labels obtained from Australian suppliers.
[3] An MSDS must be reviewed periodically to keep it up to date, for example when any new or significant information becomes available on the hazards of the material. Otherwise, an MSDS must be reviewed and re-issued every 5 years. Thus these MSDS do not comply.

Thus the majority of CNT MSDS hazard identification section and toxicology sections did not identify possible serious effects following inhalation of CNTs. These effects appear to be primarily due to the surface properties and aspect ratio of CNTs (i.e. length to width ratio) and none of the CNT MSDS included specific information on product biopersistence, dispersibility or aspect ratios. These properties are important for the hazard identification and classification of CNTs.

Most MSDS for metal or metal oxide ENMs include information on the health effects of the bulk equivalent rather than for the nano-sized material. Additionally these MSDS do not provide additional statements to contextualise the absence of ENM specific information.

- Exposure standards presented on most MSDS are those for the bulk material, with no qualification about its relevance or application to nano-sized materials.
- Only three of 50 MSDS included specific information on ecological effects (i.e. ecotoxicity results).
- Practically all the control measures provided on the MSDS were general statements that apply to bulk materials.
- 10 % of nanoparticle MSDS contained specific recommendations for local exhaust ventilation and provided details for the type of respirator to be used.

Overall 18% (9/50) MSDS were assessed as providing reliable information to appropriately inform an occupational risk assessment. Thus there is an urgent need for improvement.

Improvements to ENM MSDS can be achieved with the provision of the following guidance:

- Appropriate advice on search strategies to obtain relevant data (and frequency that such searches should be conducted)
- Interpretation of existing data for hazard identification purposes
- Hazard Classification for different types of ENMs
- Selection processes for appropriate exposure standards. For instance, Section 14 of the Exposure Standards Guidance Note [NOHSC:3008(1995)] could be expanded to include specific considerations for engineered nanoparticles
- Appropriate cautionary statements for use on MSDS in the absence of data, and
- Specific recommendations for control measures particularly engineering controls and personal protective equipment for nano-sized particulates.

Labelling

Major findings for the assessment of labels include:

- Practically all (14/15) labels included the word “nano” within the product name or product description. Laboratory reagent labels (n=9) contain the word “nanopowder” in product description and also the particle size.

- The labels reflected the content as presented on the MSDS including the inadequacies identified in relation to chemical identification and hazard classification. For instance on one label for carbon nanotubes, the name was described as "Synthetic graphite powder", an inaccurate description for a carbon nanotube.
- The labels did not contain additional cautionary notes regarding the suspected hazards of Engineered Nanomaterials (ENM). Although currently not mandatory, a cautionary note warning users that the hazards of ENMs have not been fully elucidated and emphasising the need to handle with care would be useful and relevant information.

Contents

Glossary of terms

aerodynamic diameter: Diameter of a spherical particle with a density of 1000 kg/m^3, that has the same settling velocity as the particle under consideration; related to the inertial properties of aerosol particles.

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.

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.

anthropogenic: Of human origin; man-made.

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

effective particle size: Measure of a particle that characterises its properties or behaviour in a specific system.

engineered nanoparticles: Nanoparticles between 1 nm and 100 nm manufactured to have specific properties or composition. Abbreviation **ENM**. (Working definition only – refer to other definitions with prefix “nano-“ below).

fullerene: A new allotrope of carbon characterized by a closed cage structure consisting of an even number of three coordinate carbon atoms without hydrogen atoms. This class was originally limited to closed-cage structures with twelve isolated five- membered rings, the rest being six- membered rings.

MSDS: Material Safety Data Sheet.

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

MWCNTs: Abbreviation for multi-walled carbon nanotubes.

nano: 10^{-9} or, alternatively, 0.000000001.

nanoaerosol: A collection of nanoparticles suspended in a gas.

nanocrystals: A nanocrystal typically has a diameter of between 1 and 10 nm and may contain as few as a hundred or as many as tens of thousands of atoms. Many fundamental properties of nanocrystals depend strongly on their size. Related term: **quantum dots.**

nanoengineering: The construction of nanostructures and their components.

nanofibre: Nano-object with two similar external dimensions in the nanoscale and the third dimension significantly larger. 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.

nanomaterials: Contain only a few thousand or tens of thousands of atoms, rather than the millions or billions of atoms in particles of their bulk counterparts.

nano-object: Material with one, two or three external dimensions in the nanoscale.

nanoparticle(s): Nano-object with all three external dimensions in the nanoscale. 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**.

nanophase: Discrete phase (i.e. material's physical state), within a material, which is at the nanoscale.

nanoplate: Nano-object with one external dimension in the nanoscale and the two other external dimensions significantly larger.

nanopowder: Dry nanoparticles.

nanorod: Solid nanofibre.

nanoscale: Size range from approximately 1 nm to 100 nm, but can include both bigger and smaller particles[4].

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.

nanospheres: Spheres ideally completely spherical and homogeneous in size and at the nanoscale.

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.

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

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[4] Some organisations have proposed that the size range in the definition be extended up to 300nm.

nanotubes: Hollow nanofibre.

nanowires: Electrically conducting or semi-conducting nanofibre.

national exposure standard (NES): 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).

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

occupational exposure limits: Term used to describe exposure limits or exposure standards in some countries.

particle: Minute piece of matter with defined physical boundaries.

particle size: Size of a particle as determined by a specified measurement method.

permissible exposure limit (PEL): OSHA (USA) guideline/standard for maximum workplace exposure over an 8-hour time weighted average (TWA) exposure. Equivalent to Australian NES (National Exposure Standard).

quantum dots: Crystalline nanoparticles that exhibit size-dependent properties due to quantum confinement effects on the electronic states

SDS: Safety Data Sheet.

semiconductor: Material whose conductivity is normally in the range between that of metals and insulators and in which the electric charge carrier density can be changed by external means.

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

specific surface area: Ratio of the surface area to the mass of a nanopowder.

specific surface area mean diameter: Diameter calculated from a ratio of particle volume to specific surface area adsorption (applicable for non-porous spherical nanoparticles and often carried out by the BET (Brunauer,Emmett,Teller) method).

SWCNTs: Abbreviation for single-walled carbon nanotubes.

ultrafine particles: Particle with an equivalent diameter less than 100 nm (most nanoparticles, defined by their geometrical dimensions, are ultrafine particles, when measured).

List of health effect risk phrases referred to in report [NOHSC:1008(2004)].
R20: Harmful by inhalation
R21: Harmful in contact with skin
R22: Harmful if swallowed
R23: Toxic by inhalation
R24: Toxic in contact with skin
R25: Toxic if swallowed
R26: Very toxic by inhalation
R27: Very toxic in contact with skin
R28: Very toxic if swallowed
R29: Contact with water liberates toxic gas.
R30: Can become highly flammable in use
R31: Contact with acids liberates toxic gas
R32: Contact with acids liberates very toxic gas
R33: Danger of cumulative effects
R34: Causes burns
R35: Causes severe burns
R36: Irritating to eyes
R37: Irritating to respiratory system
R38: Irritating to skin
R39: Danger of very serious irreversible effects
R40: Limited evidence of a carcinogenic effect
R41: Risk of serious damage to eyes
R42: May cause sensitisation by inhalation
R43: May cause sensitisation by skin contact
R44: Risk of explosion if heated under confinement
R45: May cause cancer
R46: May cause heritable genetic damage
R48: Danger of serious damage to health by prolonged exposure
R49: May cause cancer by inhalation
R50: Very toxic to aquatic organisms
R51: Toxic to aquatic organisms
R52: Harmful to aquatic organisms
R53: May cause long-term adverse effects in the aquatic environment
R54: Toxic to flora
R55: Toxic to fauna
R56: Toxic to soil organisms
R57: Toxic to bees
R58: May cause long-term adverse effects in the environment
R59: Dangerous for the ozone layer
R60: May impair fertility
R61: May cause harm to the unborn child
R62: Possible risk of impaired fertility
R63: Possible risk of harm to the unborn child
R64: May cause harm to breast-fed babies
R65: Harmful: may cause lung damage if swallowed
R66: Repeated exposure may cause skin dryness or cracking
R67: Vapours may cause drowsiness and dizziness
R68: Possible risk of irreversible effects

1 Scope

This review reports an evaluation of 50 Material Safety Data Sheets (MSDS) and 15 labels for products containing Engineered Nanomaterials (ENM). The evaluation is intended to consider how information on current ENM MSDS and labels reflects the state-of-knowledge in regard to the hazards, risks and controls. The report provides an assessment of the relevance, accuracy and context of the information presented on the evaluated MSDS and labels for the protection of health and safety in the workplace. In addition the evaluations consider how the ENM MSDS and labels comply[5] with the Australian National Codes of Practice for MSDS and Labelling [NOHSC:2011(2003)] and [NOHSC:2012(1994)] respectively.

In order to obtain MSDS and labels the following activities were undertaken:

- Direct requests to 20 companies for product MSDS and labels for nanomaterials
- A search of product listings of chemical companies thought to be producers of ENMs, followed by specific requests to these companies to provide MSDS and labels
- Internet searches for MSDS and labels stating that the substance contains ENM
- Literature search for literature on other evaluations of ENM MSDS and labelling
- Literature search for guidance on preparation of ENM MSDS and labels

The methodology and instruments used to evaluate individual MSDS and labels as well as a bibliographical listing of the MSDS and labels evaluated are provided in this report.

[5] Only considered for MSDS and labels obtained from Australian suppliers.

2 Purpose of MSDS and labels

2.1 MSDS

An MSDS is primarily intended to provide critical information to employers and employees about hazards of a substance and appropriate workplace controls in order to allow informed decisions about safe handling and storage. It is also intended to provide basic information about hazards and controls to assist a range of professionals such as fire fighters, ambulance officers, Environment Protection Authority (EPA) officers, State Emergency Services (SES) officers, medical personnel, regulatory officers and scientists, to understand the nature of the hazards, risks from exposure and clean-up or treatment options. Finally, they also provide information for other users (e.g. the ‘public’). For products classified as ‘hazardous’, there are statutory requirements for both MSDS and labelling. Although these requirements are non-statutory for products classified as non-hazardous they are commonly applied as good practice. This is in part explained by the general duty under most OHS Acts that the employer must provide adequate information on substances to ensure the safe use, handling and storage of these substances.

A Code of Practice for the preparation of MSDS[6] has existed in Australia since 1994. The second edition, effective since 2003, aligned Australian requirements with those overseas, in particular with the 16 header format adopted by the European Union and the International Labour Organisation. It also incorporated the information provisions of the Dangerous Goods standard. It was also seen as an opportunity to prepare for future alignment of Australian requirements with the Globally Harmonised System of Classification and Labelling of Chemicals (GHS).

It is requirement under Commonwealth, State and Territory regulations that employers must obtain and make available to all employees, MSDS for all hazardous substances and/or Dangerous Goods supplied or used in the workplace. MSDS are seen as a recognised information source which allows risk management decisions to be made in the workplace.

In a strict regulatory sense the Code of Practice applies to materials classified as a) hazardous substances, and/or b) Dangerous Goods, however it serves as the primary guidance document for the preparation of MSDS for all chemical preparations regardless of their hazard status.

The 16 header MSDS contains the sections given in Table 2.1.

[6] The current edition is the second edition: *National Code of Practice for the Preparation of Material Safety Data Sheets 2nd Edition* [NOHSC: 2011 (2003)] and came into effect 24 April 2006.

Table 2.1: Summary of Australian MSDS requirements

Section	Description	Core Information
1	Identity of material and supplier	• Product name • Other names • Recommended use • Supplier name, address, telephone number, and Australian emergency contact number
2	Hazards identification	• Hazard classification, including statement of overall hazardous or dangerous nature • Risk phrases • Safety phrases
3	Composition and information on ingredients	*Pure substances* • Chemical identity of pure substances • Common names and synonyms • CAS numbers *Mixtures or Composite Materials* • Chemical identity of ingredients • Proportion of ingredients • CAS Number of ingredients
4	First aid measures	• Description of necessary first aid measures according to routes of exposure • Indication of medical attention and special treatment needs
5	Fire fighting measures	• Suitable extinguishing media • Hazards from combustion products • Precautions for fire fighters and special protective equipment
6	Accidental release measures	• Emergency procedures • Methods and materials for containment and clean up
7	Handling and storage	• Precaution for safe handling • Conditions for safe storage including any incompatibilities
8	Exposure controls/ personal protection	• National exposure standards • Biological limit values • Engineering controls • Personal protective equipment
9	Physical and chemical properties	• Clearly identify the physical and chemical properties such as melting points, boiling points, solubility, specific gravity etc
10	Stability and reactivity	• Chemical stability • Conditions to avoid • Incompatible materials

Section	Description	Core Information
		• Hazardous decomposition products • Hazardous reactions
11	Toxicological information	• Acute and chronic health effects • Possible routes of exposure • Range of effects following exposure • Doses, concentration or conditions likely to cause injury • Delayed effects • Relevant negative data
12	Ecological information	• Ecotoxicity • Persistence and biodegradability • Mobility
13	Disposal considerations	• Disposal methods, including disposal of container • Special precaution for landfill or incineration
14	Transport information	• UN Number • UN Proper Shipping Name • Class and subsidiary risk(s) • Packing group • Special precaution of users • Hazchem Code
15	Regulatory information	• Regulatory status of material under relevant Australian health, safety and environment legislation including: o TGA Act o APVMA Act o ICNA Act
16	Other information	• Date of preparation of MSDS • Data sources • Literature references • Key/legend of abbreviations and acronyms

The third revised edition of the GHS was published in early July 2009. It contains both hazard classification and hazard communication (SDS and labelling) requirements. Following its publication Safe Work Australia released a draft of the 3rd edition of the National Code of Practice for the Preparation of Safety Data Sheets (SDS Code of Practice) on 31 July 2009 (Safe Work Australia 2009b) together with a policy proposal for *Workplace Chemicals Model Regulations* (Safe Work Australia 2009a). The draft Code of Practice does not contain specific requirements for engineered nanomaterials however it does rely on hazard classification of the 3rd revised edition of the GHS. The GHS contains a new set of hazard classification criteria to those previously used in Australia. Also it contains guidance regarding inclusion of non-mandatory chemical and physical properties for chemicals with novel properties. Some of these are highly relevant to ENMs including; particle size (average and range), shape and aspect ratio, crystallinity, dustiness, surface area, degree of aggregation, biodurability or persistence.

Implementation of this SDS Code of Practice will facilitate the introduction of GHS-consistent overseas SDS into Australia and assist Australian exporters to provide GHS-consistent safety information to overseas markets[7]. The new criteria contain more flexibility to the classifier to classify substances in the absence of toxicity testing. The flexibility is encoded within guidance on how to apply expert judgement to derive a hazard classification. *In vitro* toxicity testing and predictive tools based on existing information for analogous substances can be used within an expert judgement to derive a classification. It is expected that the GHS guidance on expert judgment will allow for precautionary hazard classifications for ENMs to be derived.

Consistent with the above points, the policy proposal for Workplace Chemicals Model Regulations (Safe Work Australia 2009a) published in July 2009 contains the following note:

> *Manufactured nanomaterials may require a different classification and hazard communication elements (labelling and SDS) compared to the macro-form of the same material* (Section 4 Definitions pg 23)

In support of this note the draft revised Australia Criteria for Classification of Hazardous Substances includes guidance on the classification of ENMs. The guidance requires classifications to specifically consider ENM specific characteristics such as size, shape, number concentration, surface area, charge and overall surface reactivity. Given the limited understanding of the characteristics of nanomaterials, the Australian Criteria also recommend that the hazard assessment of ENMs should be done on a case-by-case basis.

2.2 Labels

Labels contain critical information required to transport, handle and store substances in a safe manner and in conformance with both international and national regulatory requirements. In addition they are intended to provide contact points and critical information (hazard phrases on human health and environment, first aid and clean up advice) to allow personnel to act quickly to initiate an emergency response.

The *National Code of Practice for the Labelling of Workplace Substances* [NOHSC:2012(1994)] was introduced to codify a standardised national labelling approach to allow Australian manufacturers and importers of substances to meet their requirements to Australian regulations and codes (i.e. State based Dangerous Goods, Poisons and Occupational Health and Safety legislation)[8].

A label is broadly defined by the Code of Practice as any information on a container which identifies the substance in the container and provides basic information about its safe use and handling.

[7] GHS implementation has begun, and is at various stages, in most countries around the world.
[8] A number of complementary labelling systems exist in Australia; agricultural and veterinary medicines, therapeutic goods, foods, cosmetic products, munitions and explosives. These labelling systems were not considered within this report.

Workplace hazardous substances may be labelled in accordance with overseas requirements provided the labels have equivalent information to that advised in the national Code of Practice.

The information required on Australian workplace labels is summarised in Table 2.2. The size of the container dictates the level of information required. All information on an Australian label should be on the outside face of the containers, in English, in durable print and a lettering size and style which is easily legible.

Safe Work Australia (2009c) released a revised draft Labelling Code of Practice in July 2009 in order to facilitate the local implementation of the Globally Harmonized System of Classification and Labelling of Chemicals (GHS) for workplace hazardous chemicals in 2009. The GHS provides harmonised hazard communication elements for use on labels and SDS. The GHS includes new hazard phrases, and hazard pictograms containing symbols (diamonds consistent to those used for the transport of dangerous goods). The label is intended to convey information about acute and long term (chronic) health hazards, physical hazards and environmental hazards in a simple standardised format.

Table 2.2 Australian label requirements

Information needed for container with a capacity more than 500 mL(g)	**Information needed for container with a capacity of 500 mL(g) or less [a]**
Signal words and/or dangerous goods class and subsidiary risk label(s) (where applicable)	Signal words and/or dangerous goods class and subsidiary risk label(s) (where applicable)***
Identification information including 1)product name, 2)chemical name, 3)UN number, 4)ingredient and formulation details (where relevant)	Identification information including 1)product name***, 2)chemical name
Risk phrases	Risk phrases (at least the most significant ones)
Direction for use (where appropriate)	Not needed
Safety phrases	Safety phrases (at least the most significant ones)
First aid procedures	First aid procedures
Emergency procedures	Not needed
Details of manufacturer or importer	Details of manufacturer or importer***
Expiry dates (where relevant)	Not needed
Reference to MSDS	Reference to MSDS

[a] Where the container is so small that this information cannot be provided the containers should be marked with items denoted with "***" in Table 2.2.

3 Evaluation methodology for ENM MSDS and labels

3.1 Evaluation of ENM MSDS

The evaluation of MSDS has the following objectives:

- Evaluate whether the MSDS contains relevant accurate and contextual information with regard to the hazards, risks and controls associated with the specific ENM
- Evaluate compliance with Australian National Code of Practice for the Preparation of Material Safety Data Sheets 2nd Edition [NOHSC:2011(2003)].

The evaluation is intended to identify:

- good practices
- accuracy of information
- whether the information includes specific attention to ENM properties, hazards and controls
- important deficiencies
- data gaps, and
- other issues.

3.2 Evaluation of ENM specific information and advice

Appendix 1 provides the proforma for the evaluation checklist used to review individual MSDS. A separate checklist for labels was not generated and the information on labels was evaluated on a case-by-case basis using the same evaluation criteria as those for MSDS.

In the absence of standard terms for the quality assessment of MSDS and labels the following definitions were used in the present report:

Reliability	Was used in the context of evaluating the overall quality of the MSDS or label relating primarily to the relevance and accuracy of information presented.
Relevance	An assessment of how relevant information in each section is to the engineered nanomaterial (i.e. representative of properties, hazards or controls). Either a descriptor of N/A (not applicable) or a rating of between 1-5 is entered (1 no relevance, 2 little relevance, 3 some relevance, 4 mainly relevant, 5 highly relevant).
Accuracy	Was assessed by considering the information presented and either; prior knowledge of a property, or inconsistencies for a property between different sections of the MSDS. For example if:

- the occupational exposure standard for nuisance dust is applied to a carbon nanotube, or
- first aid recommendations and toxicology data provided are inconsistent with hazard and risk phrases presented in Section 2.

Accuracy was assessed on a case by case basis. Accuracy was rated as 1= inaccurate, 2= partially accurate, 3= accurate.

In order to evaluate whether the information and advice on MSDS and labels for ENMs is relevant, accurate and contextual requires an understanding of what information and advice is pertinent and currently available.

Given that the hazard characterisation of ENMs is still underway and much of the test requirements are still being formulated and standardised, there are gaps in the knowledge necessary for creating and populating an MSDS (OECD 2006, Norden 2007, BSI 2007, Safe Work Australia 2009b).

However over the past 10 years a large database of primary studies investigating the chemical and physical properties, health effects and environmental effects of ENMs has become available. These studies are being periodically reviewed to update understanding of hazard and to a lesser extent risk. These reviews to-date have raised potential concerns regarding health hazard and risks, with concerns that relate to lack of hazard information for specific engineered nanoparticles (ENPs), and the concerns arise because there is a dearth of inhalational and long term toxicological studies (Ostinguy et al. 2006, Health Council of the Netherlands 2006, SCENIHR 2006, DEFRA 2007, SCCP 2007, US EPA 2007, UK Royal Commission 2008). In addition, there are new studies being undertaken and added to the database continually.

The long time frames required to produce relevant test protocols, and conduct testing in order to gather the necessary data for meaningful risk assessments necessitates the need for precaution when handling ENMs. This is no different from any other material for which there is minimum information on health effects.

In light of current understanding several organisations have specifically considered what constitutes appropriate information and advice on health and safety for ENMs (BSI 2007, ISO 2008b). From these reviews a number of ENM specific considerations were used to guide the evaluation of good practice, accuracy and relevance. The ENM specific considerations assessed include; identification of the ENM and hazard identification.

Identification of the ENM

Traditionally chemical substances are identified by either a product name, common or scientific chemical name depending on their hazard classification. Australian rules for naming ingredients on MSDS and labels are tiered depending on whether a substance is non hazardous or hazardous and for hazardous substances the severity of the health hazard [NOHSC:2011(2003)].

For some hazardous substances (those classified as R23, R24, R25, R26, R27, R28, R34, R35, R39, R40, R42, R43, R45, R46, R48, R49, R60, R61, R62, R63, R68) chemical names and CAS numbers are required, while for relatively low hazard substances (R20, R21, R22, R31, R32, R33, R36, R37, R38, R41, R64, R65) only generic names are required.

Other than for fullerenes no systematic (chemical entity) naming or classification scheme is currently available for ENMs (European Commission 2008, Powell et al. 2002, Godly and Taylor 1997, Cozzi et al. 2005).

The lack of a coherent nomenclature can be confusing when attempting to interpret the hazards and risks associated with ENMs. Engineered nanomaterials are presented in a wide range of forms. Recently categorisation systems have been developed to assist in hazard identification (ISO 2008a, ISO/TS 27687). The categorisation systems provide three divisions for ENMs (defined as 'nano-objects'; nanoparticles, nanofibre, nanoplate – see Glossary for definitions). Hansen et al. (2007) linked these divisions to data items to characterise hazards.

Taking the above into consideration when assessing MSDS we asked the following questions:

- Does the MSDS or label identify the presence of a nano-object?
  For hazardous substances, does the generic or specific chemical name allow the reader to distinguish nanoscale materials with bulk materials?

Hazard Identification

The following properties will assist the evaluation of whether the hazard classification and also the control measures recommended in the MSDS are appropriate. It is not intended to be a thorough review of such properties rather a guide to MSDS evaluators for key properties and supporting test data:

- For all nano-objects, is a qualitative description of the object size and form provided?

- For nanoparticles is a qualitative or quantitative characterisation of form & size provided?

  Some insoluble fibrous particles on entry into alveolar regions of the lungs cannot be removed by lung clearance mechanisms and are highly persistent due to their insolubility. Thus they remain in the lung for long periods of time resulting in inflammation and related diseases. Mercer et al. (2008) showed SWCNTs are able to penetrate deep into the lung after pharyngeal aspiration to mice. The preliminary data of Hubbs et al. (2009) and Bonner et al. (2009) appears to support that, after either pharyngeal or inhalation exposure, MWCNTs can penetrate through to the pleural mesothelial tissue and cause lesions.

  Thus it is necessary[9] to identify such materials or similar on the MSDS. This can be done in a qualitative sense (e.g. identified as a long thin fibre of nanosized carbon tubules) or quantitative fashion (needle like fibre, fibre length and particle diameter, particle distribution).

[9] Necessary, in order to allow employers to comply with their general duties under the National Code of Practice and State/Territory legislation.

- For nanoparticles, does the MSDS provide information on dispersion?

  Agglomeration of nanoparticles appears to give rise to lesser pulmonary toxicity than dispersions of the original nanoparticle. For any particular NP the relevance of the data for human health will depend upon whether workers are exposed primarily to dispersed nanoparticles or to agglomerates. Sayes et al. (2007) found the aggregation state of different NPs varied according to the dispersion medium. For fine ZnO and nano-ZnO, the size distribution of particles was much greater in phosphate buffered saline (PBS) than either water or culture media. In water the median size of anatase UF TiO_2 was 129 nm, but in PBS it was 2,961 nm (Warheit et al. 2007). Information on dispersion is often contained in technical materials provided to customers.

  It is however noted that an agreed dispersion protocol has not been established making it difficult to standardise the presentation of such information.

- For nanoparticles or other ENMs, does the MSDS provide information on the likelihood of the material to cause ignition, sparking, reactivity?
  - Description of the dustiness of the material can inform controls and categorisation as a dust explosion hazard
  - Self ignition temperature and method used to perform test
  - Minimum ignition energy and method used to perform test
  - Incompatible substances
  - Hazardous reactions and conditions for such reactions to occur

  Such substances may have the propensity for categorisation as explosive, flammable or combustible depending on the conditions required to cause the reaction.

- Are results of toxicity studies (including test method) or a summary of toxicity information presented justifying the health hazard classification?

- Is the information on the MSDS sufficient to inform the reader of its environmental hazard?

  Formal consideration in Australia of environmental hazard is a requirement according to the recently released seventh edition of the Australian Dangerous Goods Code (NTC 2007)[10].

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[10] In the MSDS Code of Practice (Section 6.12), in regard to regulatory requirements on the provision of ecological information, it states: *Provision of ecological information is a requirement of the GHS. At the time of publication of this code, there is no consistent national requirement under the Commonwealth, State and Territory hazardous substances regulations to provide this information. However, under Dangerous Goods regulation, some States and Territories require this information* (NOHSC 2003).

The draft SDS Code of Practice (Safe Work Australia 2009b) states (Section 5.12): *At the time of publication of this code, there is no consistent national requirement under the Commonwealth, State and Territory hazardous chemicals OHS regulations to provide information on environmental hazards on SDS. However if a hazardous chemical has been classified as environmentally hazardous, then this information should be included in the SDS to satisfy the manufacturer's common law duty of care.*

Nanoparticles, because of their smaller size and dispersion properties, are likely to have different environmental fate and effect properties.

- Is the ENM accurately classified according to the Approved Criteria for Classifying Hazardous Substances (HS), the Australian Dangerous Goods (DG) Code and the Standard for Uniform Scheduling of Drugs and Poisons (SUSDP), if applicable?

  While the Approved Criteria applies to chemicals generally, including ENMs, currently there is no specific detailed guide to the classification (DG, HS or SUSDP) of ENMs.

  Some nanoparticles, but not all, are more toxic than their bulk counterpart due to differences in properties such as greater surface area and expected higher surface reactivity. For instance, following chronic inhalation lung tumours have been observed in rats with fine (<2.5 μm) titanium dioxide (TiO_2) at 250 mg/m^3 and ultrafine (<0.1 μm) TiO_2 at 10 mg/m^3, but not in mice or hamsters (Lee et al. 1985a, 1985b, 1986; National Toxicology Program, 1993; Heinrich et al. 1995; Nikula et al. 1995). As a precautionary default all biopersistent CNTs, or aggregates of CNTs, of fibre dimensions could be considered as presenting a potential fibrogenic and mesothelioma hazard unless demonstrated otherwise by appropriate tests (Safe Work Australia 2009).

- For ENMs classified as non hazardous what information is contained on the MSDS to support the classification?

  Several reviewers have suggested that all nanoparticles should be considered as potentially hazardous in the absence of specific information to conclude otherwise (BSI 2007, Maynard et al. 2006, NIOSH 2009).

- For ENMs present in ambient air, has a suitable exposure standard been identified?

  Currently there are only a small number of specific limits for airborne exposures to engineered nanoparticles, although for some engineered nanomaterials with no specific limits, occupational exposure limits exist for larger particles of similar chemical composition. It must be recognised that exposure limits recommended for non-nanoscale particles are most likely not health protective for nanoparticle exposures (e.g., the Exposure Standard for graphite or bulk titanium dioxide is not a safe exposure limit for carbon nanotubes or nano-titanium dioxide) (BSI 2007, NIOSH 2009a, NIOSH 2005).

- Does the MSDS contain specific control procedures for the substance in nano form? Particularly for:
  - foreseeable processing that may result in generation of dust or aerosols (e.g. aerosolisation during manufacturing or spray coating), and
  - transfer, mixing, filling, scooping of material (dusts, suspensions capable of forming aerosols).

Although it may be difficult to include detailed specific recommendations for control measures for ENM on MSDS, and these would be identified by a site specific risk assessment for each workplace [NOHSC:3017 (1994)], general recommendations to reduce exposure should be included where possible.

Currently there is a lack of sufficient data and evidence to provide specific guidance for nanoparticles for many MSDS items including: medical screening and interventions, cleanup and disposal, and personal protective equipment (NIOSH 2009a). This should be noted on the MSDS and a precautionary approach to exposure should be recommended. In addition, due to ever-increasing research, companies should review MSDSs regularly.

For exposure prevention as well as fire, explosion and catalysis prevention and control, much of the existing advice for the effective control of powders, aerosols and gases in industrial facilities also apply to ENM (Harford 2007, BSI 2007, NIOSH 2009a).

3.3 Evaluation of labels

The evaluation of labels has the following objectives:

- Evaluate whether the label contains relevant accurate and contextual information specific to the ENM (where appropriate)
- Evaluate compliance with Australian National Code of Practice for the Labelling of Workplace Substances [NOHSC:2012(1994)]

In order to achieve these objectives the following questions were asked:

- Does the label identify that the product contains a nanomaterial?
- Does the label contain appropriate hazard statements?
- If an Australian supplier, does the label comply with [NOHSC:2012(1994)]?
- Does the label advise on exposure control (dust or aerosol generation, ventilation)?

3.4 Compliance with Australian requirements

Each MSDS was assessed for its compliance with the *National Code of Practice for the Preparation of Material Safety Data Sheets 2nd edition* [NOHSC:2011(2003)] (MSDS Code). Non conformances to each section of the MSDS were subcategorised as “major” or “minor” non conformances based on whether the non conformance related to a requirement or recommendation in the MSDS Code. For overseas MSDS, compliance against the MSDS Code was not considered[11] for the following items:

- Australian contact details
- Compliance with Australian specific ingredient disclosure requirements
- Australian classifications and exposure standards

Refer to Appendix 1 for the checklist.

[11] The checklist list item in these cases were marked “Not Applicable”.

4 Summary of MSDS and labels obtained

In total 50 MSDS and 15 labels were obtained for a variety of different forms of engineered nanomaterials (ENMs) as summarised in Table 4.1. The MSDS and labels obtained were allocated a unique number, and the MSDS number along with the type of nanomaterials is provided at Appendix 2. Most product MSDS reported the product to be classified as hazardous[12] (82%) and were produced in Australia (36%). The MSDS were obtained from three major sources; product manufacturer/distributors, local users (i.e. users of research material or raw material) and the internet.

A formal analysis of the representativeness of the ENM MSDS and labels obtained was not conducted. However Figures 4.1 through to 4.5 below provide an overview of the categorisation of the MSDS and labels obtained.

Table 4.1: No. of MSDS and labels obtained by ENM type

Type of ENM	Number of MSDS
Metals and metal oxides	17
Silicates	7
Carbon nanotubes	12
Other	14
Total	**50**

Type of ENM	Number of Labels
Metal oxides	4
Silicates	5
Carbon nanotubes	3
Other	3
Total	**15**

Type of ENM	Number of MSDS
Nano tubes and nanofibres	13
Nanoparticle (solid)	18
Nanoparticle dispersed in solution or paste	19
Total	**50**

[12] Some overseas MSDS that contained hazard statements in section 3 but were not classified according to [NOHSC:1008(1999)] were considered to be classified as hazardous.

Use Category	Number of MSDS
Cleaning products	1
Personal Care products (e.g. dermatological treatments, dental care, sunscreen ingredients)	0
Surface coating formulation (ingredients for formulating paints)	15
Printing industry	3
Electronics industry	4
General industry/Not stated	27
Total	**50**

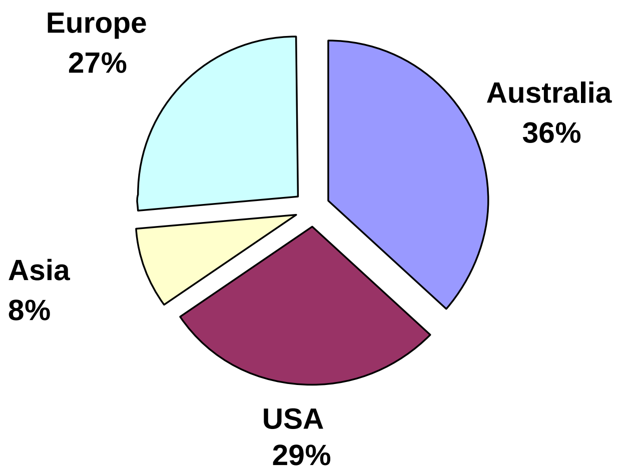

Figure 4.1: Pie Chart showing percentage of total MSDS grouped according to place of origin.

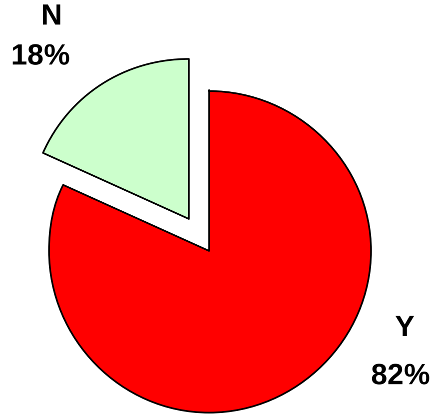

Figure 4.2: Pie Chart showing percentage of total MSDS where nanomaterial was categorised as hazardous (Y) and non-hazardous (N). The "N" group also includes those MSDS where no statement was made regarding the hazard.

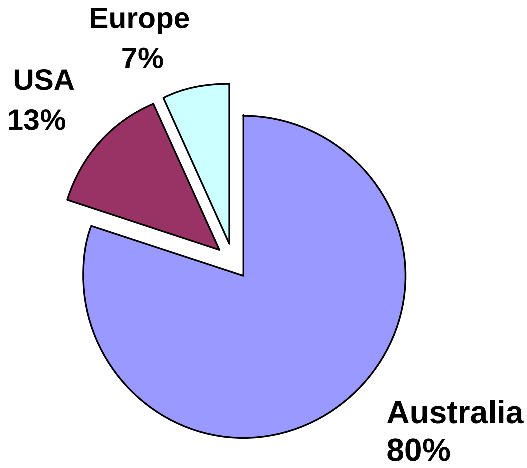

Figure 4.3: Pie Chart showing percentage of total labels grouped according to place of origin.

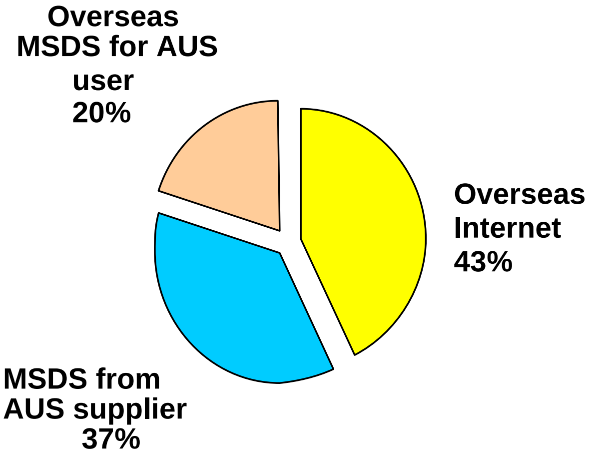

Figure 4.4: Pie Chart showing percentage of overseas MSDS found on the internet, overseas MSDS found on the internet intended as the source of supply to Australian users (i.e. website allows selection of MSDS by country or region), as well as MSDS from Australian suppliers.

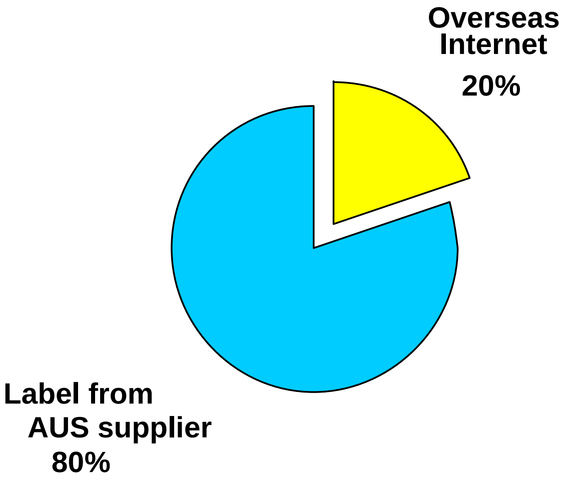

Figure 4.5: Pie Chart showing percentage of overseas labels found on the internet, as well as labels found on the internet or received from Australian suppliers.

5 Evaluation results for MSDS

5.1 Summary of results

On most MSDS examined, products were classified as hazardous (82%) and the most frequent classification (60% of those classified as hazardous) for engineered nanomaterials (ENM) was as an irritant (R36/R37). Three MSDS (including an unpublished model MSDS for silver) included a classification based on serious effects after repeat or prolonged exposure via inhalation (GHS Target Organ Toxicity Category 1, roughly equivalent to R48/R23; Danger of serious damage to health by prolonged exposure through inhalation).

Of those produced in Australia (36%), 89% conformed with the Australian Code of Practice for Preparation of MSDS [NOHSC:2011(2003)].

Overall 18% (9/50) of MSDS were assessed as providing an adequate and accurate description sufficient to inform an occupational risk assessment. Most products did not provide ENM specific descriptions and data.

Practically all the control measures provided on the MSDS were general statements that apply to bulk materials and without evidence to the contrary, it is unlikely that the same advice is relevant to ENMs. 13 % of nanoparticle MSDS contained specific recommendations for local exhaust ventilation and provided details for the type of respirator to be used.

Evaluation results are presented for four groupings of ENM namely; carbon nanotubes, metals and metal oxides, silicon compounds including oxides, and others.

5.2 Carbon nanotubes (CNTs)

Tables 5.1 and 5.2 provide a summary of carbon nanotube (CNT) MSDS evaluation. Twelve MSDS for CNT were available for review, one prepared in Australia and the remainder prepared overseas (USA (6), China (2), India (1) and Europe (2)). Eleven of 12 MSDS was presented in the ILO format, and one MSDS was presented in accordance with the Australian Code of Practice. Two of the 11MSDS prepared overseas were supplied by an Australian research organisation as overseas supplier MSDS. The Australian MSDS evaluated complied with Australian specific requirements[13] for MSDS and not surprisingly the overseas MSDS did not.

The Australian MSDS was different to practically all other MSDS for CNTs evaluated as it characterised the hazards of CNT accurately.

Although all CNTs were classified as hazardous substances, eleven out of twelve MSDS described the hazards of CNTs to be equivalent to that of graphite. This assumption is not in line with currently available reviews and scientific studies on the health effects of CNTs.

[13] Australian contact details, Australian hazard/regulatory classifications, ingredient disclosure, exposure standards

Table 5.1 Evaluation results for carbon nanotube MSDS

Item	Result / Statistic	Comment
Number of MSDS [a]	12	
Proportion classified as hazardous	100%	All MSDS were classified as hazardous and with the exception of one described the hazards as irritating to eyes and respiratory system (R36/37) or skin, respiratory system and eyes (R36/37/38).
Proportion of MSDS considered to provide reliable (adequate and accurate) description of hazard.	8%	One of the MSDS classified CNTs as R48 or R40 [b] (refer text). All except one provided exposure standard for graphite.

[a] MSDS evaluated were primarily from overseas suppliers, thus the proportion conforming to the MSDS Code of Practice [NOHSC:2011(2003)] is not reported.
[b] Risk phrases for hazard communication, R40 = Limited evidence of a carcinogenic effect, R48 = Danger of serious damage to health by prolonged exposure.

Table 5.2 Reliability[a] evaluation for CNT MSDS

Section	Reliability
Accurate hazard classification?	8%
Includes specific chemical and physical properties? (Dispersibility, particle size)	20%
Specific ENM toxicology data provided?	25% (3/12) 2 MSDS included supplementary information on recent literature, 1 MSDS provided a URL for readers to do their own research

[a.] **% of MSDS with relevance rating of 3-5 & accuracy rating 2-3.** Relevance was rated between 1 (poor) to 5 (highly) and accuracy was rated between 1(inaccurate) and 3 (highly accurate). Refer Appendix 1 and Section 3.

Only one MSDS included the following risk phrase and text:

> *R68/20 Harmful: possible risk of irreversible effects through inhalation (limited evidence*).

The risk phrase was accompanied by a cautionary note in Section 2:

> *Note: Although there is a lack of conclusive information on the toxicity of carbon nanotubes research does show that carbon nanotubes have the potential to be harmful to health. Due to these uncertainties it is therefore recommended that all carbon nanotubes be treated as presenting a potentially significant hazard unless clear evidence to the contrary is obtained*

The hazard identification section and toxicology section for most MSDS evaluated did not identify possible serious effects following inhalation of CNTs. These effects appear to be primarily due to the surface properties, length and aspect ratio of CNTs (i.e. length to width ratio).

None of the MSDS included information on biopersistence, dispersibility or aspect ratios. The above classification and hazard description accurately reflects the potential hazards of CNTs in the absence of safety testing information to the contrary.

The remaining eleven of twelve MSDS only included the risk phrases R36 and R38, (irritating to skin and eyes). None of these MSDS provide evidence in support of the irritant classification. It is also noted that carbon-based nanomaterials, fullerenes and CNTs, have not produced any notable irritant responses in clinical patch test or rabbit ocular toxicity studies (Stern 2008, Huczko & Lange 2001, Huczko et al. 1999, Nielson et al. 2008). Relating to this finding, it is noted that the information presented on the MSDS evaluated is likely to be inaccurate.

Experimental studies in rodents have demonstrated that instillation of multi-walled and single-walled CNTs can cause pulmonary inflammation, granulomas, and fibrosis (Safe Work Australia 2009, Donaldson et al. 2006, Lam et al. 2006, Stern 2008). Although there is continuing debate about whether the experiments conducted (instillation into the lungs) are representative of physiological inhalation exposures there is a consensus that a precautionary approach to the hazard and risk assessment of CNTs is required.

Other important findings include:

- All MSDS identified the material to be a carbon nanotube (Section 1, Product name or Section 3 chemical name)
- The type (single-walled, multi-walled) of CNT was not described in most products (66%, 8 of 12)
- Three (25%) MSDS described the chemical name or CAS Number to be graphite (inaccurate description)

- 83% (10/12) MSDS incorrectly included the exposure standard for graphite. The exposure standard (ACGIH 2009, Safe Work Australia 2009) for graphite is not applicable to CNT[14]
- Two MSDS (one from China and one from Australia) provided supplementary information on CNT or fibre toxicity, physicochemical hazards and ecological hazards
- Ecological effects. The MSDSs do not provide information on ecological effects and practically all state that the information is not available
- Ventilation requirements were not described in detail. Very few MSDS mention local exhaust ventilation systems although a couple of MSDS did specify fume cupboard requirements.

5.3 Metals and metal compounds

Seventeen MSDS for metal compounds or metal oxides (referred to as "metal MSDS") or preparations containing a metal or metal compound were reviewed. The compounds reviewed included; cadmium selenide, zinc sulphide, zinc oxide, zinc sulphide, lanthanum, alumina, lead sulphide, gold, titanium dioxide, silver, strontium ferrite, tantalum, yttrium oxide and zirconium silicate. Nine of the MSDS were for nanoparticles dispersed in solution or present as a paste. Three of the MSDS were for preparations that contained 'dots' (most likely quantum dots (QDs)) in a solvent. Structurally, QDs consist of a metalloid crystalline core and a "cap" or "shell" that shields the core and renders QDs bioavailable. Cores of QDs consist of a variety of metal complexes such as semiconductors, noble metals, and magnetic transition metals (Safe Work Australia 2009). These materials can have very different physicochemical properties to nano sized metal powders.

The findings for MSDS of products containing metal oxide/compound ENMs are summarised in Table 5.3 and 5.4.

Table 5.3 Evaluation results for MSDS of metal ENM

Item	Result / Statistic	Comment
Number of MSDS	17	
Proportion conformance with MSDS Code of Practice [NOHSC:2011(2003)]	100%	Out of 17 metal and metal compounds MSDS, 8 were from Australia. All of them complied with the MSDS Code of Practice
Proportion classified as hazardous	76% (13/17)	Several discrepancies noted refer text below
Proportion of MSDS considered to provide reliable (relevant and accurate) description of hazard.	47% (8/17)	Refer 5.4

[14] A recent Safe Work Australia report on the toxicology of Engineered Nanomaterials recommended "consideration be given to establishing an occupational exposure standard for CNTs. Since current optical microscopy methods for counting asbestos fibres are inadequate for CNTs, a method of counting CNTs would also need to be considered."

Table 5.4 Reliability [c] evaluation for MSDS of metal and metal compound ENM

Section	Reliability
Relevant and accurate hazard classification [a]?	47% (8/17)
Exposure Standard[b]	41% [d] (7/17)
Includes specific physicochemical properties? (Dispersibility, particle size)	18% (3/17)
Specific ENM toxicology data provided?	24% (4/17)

a. Assessed primarily on the consistency of information between the hazard classification and other sections of the MSDS particularly the health hazard sections presented in the MSDS.
b. 9 MSDS were for metal nanoparticles dispersed in liquids or presented as a paste - the question was not evaluated for these ENMs.
c **% of MSDS with relevance rating of 3-5 & or accuracy rating 2-3.** Relevance was rated between 1 (poor) to 5 (highly) and accuracy was rated between 1(inaccurate) and 3 (highly accurate) Refer Appendix 1 and Section 3.
d. Where an exposure standard existed for a metal compound for respirable dust levels. These exposure standards are not strictly specific to ENMs however were considered to be relevant in the absence of information to the contrary.

Key observations made on the MSDS for metals and metal oxide ENM include:

- All MSDS described the product (product name or product description in section 1) as a “nano” or “nanoparticle”.

- Most products include information on the health effects of the bulk equivalent rather than for the nano-sized material. Additionally these MSDS do not provide additional statements to qualify the information provided. However MSDS Number #4 provides an example of good practice in this regard:

  > *To the best of our knowledge the acute and chronic toxicity of this substance is not fully known. Cadmium Selenide in the form of a nanocrystal may or may not present the same health hazards as larger cadmium or selenium containing molecules. It is therefore encouraged to use caution when handling this product as its toxicity and modes of exposure are not well characterised or understood.*

  Two MSDS were available for nanosilver (one of which was a model MSDS). One of these was prepared in May 2007 and considered nanosilver to be a skin and eye irritant. The second MSDS prepared in November 2008 correctly classifies nanosilver as “*Target Organ system toxicity following repeat exposure, Category 1”* (equivalent to R48 - Danger of serious damage to health by prolonged exposure). The basis for the classification is a 90-day whole body repeat dose inhalation experiment with rats exposed to approximately 49 μg/m^3, 133 μg/m^3, and 515 μg/m^3 silver nanoparticles (average diameter 18–19 nm) (Sung et al. 2009). The no observed adverse effect level (NOAEL) was identified by the authors as 100 μg/m^3 which is equal to the Australian exposure standard for silver metal of 100 µg/m^3 and higher than the exposure standard for soluble silver compounds (10 µg/m^3).

- Exposure standards presented on most MSDS are those for the bulk material with no qualification about its relevance or application to nano-sized materials.

  For titanium dioxide (insoluble nanomaterial of low toxicity) NIOSH has proposed an exposure standard of 0.1 mg/m^3 for ultrafine particles versus 1.5 mg/m^3 for fine titanium dioxide (NIOSH 2005).

  Although there is little dependable information about the hazard of nanoscale alumina, historically occupational exposure to fine alumina dispersed in mineral oil (generally less than 1 µm) has been associated with pulmonary fibrosis under certain circumstances (WHO 1997, Section 8.2). This finding illustrates that both size and form of nanoparticles can influence the relative toxicity.

- Although a systematic review of product specification sheets and other technical literature was not undertaken during the MSDS and label evaluation, such literature was accessed from time to time. It is evident that details such as particle size, surface area, pore size and volume, particle size and shape and dispersibility are often available in accompanying technical literature but are not transposed in the physicochemical property sections of MSDS. For example a simple “Google” search on the product name for one MSDS (MSDS for a zinc oxide in an aqueous solution) identified a technical data sheet that states: “Dispersion into primary particles and stabilised against reagglomeration”. The description is highly relevant to the hazard and risk assessment of finely dispersed zinc oxide (aerosol formed from spray gun).

- 6% of MSDS (1/17) contained ecotoxicity testing data. However all MSDS did present cautionary (regarding the lack of data and need for exposure control) statements in the absence of such data. MSDS #37 states the acute toxicity to *Daphnia pulex* (freshwater invertebrate) to be 40-60 µg/L and identifies the GHS classification as acute toxicity category 1. However, because the EC_{50} is less than 1 mg/L and nanosilver is non biodegradable, the correct classification should be chronic toxicity category 2. Furthermore the ecotoxicity test result suggests that the product is classifiable as a Dangerous Good, Class 9 UN 3088 Environmentally Hazardous Substance.

5.4 Silicon compounds

For silicon carbide and nitride there are *in vitro* and intratracheal toxicity studies available suggesting that fibrous particles may cause severe pulmonary effects (Svensson et al. 1997, Fisher et al. 1989). The evaluated MSDS for silicon nitride did not include a description of these studies or the crystalline, fibrous nature nor is a particle size or any other information on the nanoparticles provided. However the particle size and shape (spherical) is reported on the product data sheet. Overall the MSDS did not provide a cautionary approach in describing the health hazard potential for silicon nitride.

Similarly recent results for amorphous silica nanoparticles suggest that transient fibrotic effects can occur at high doses (Choi et al. 2008). Information on the repeat dose toxicity for amorphous silica nanoparticles was not provided on the MSDS, and therefore it is not possible to conclude whether the hazard identification presented (MSDS # 40 and #41) is accurate.

The findings for MSDS of products containing silicate ENMs are summarised in Table 5.5 and 5.6.

Table 5.5 Evaluation results for silicate MSDS

Item	Result / Statistic	Comment
Number of MSDS	7	Diverse range of nanoparticles.
Proportion conformance with MSDS Code of Practice [NOHSC:2011 (2003)]	100%	All MSDS for silicates were from Australia and all of them complied with the MSDS Code of Practice
Proportion classified as hazardous	71% (5/7)	Hydrophilic fumed silica was not classified as hazardous.
Proportion of MSDS considered to provide reliable (relevant and accurate) description of hazard.	0%	0%

Table 5.6 Reliability (Relevance & Accuracy)[a] results for key MSDS Sections for silicates

Section	Reliability [a] % of evaluated MSDS
Section 2 Hazard ID Accurate hazard classification	0% (0/7) Refer text
Section 8 Exposure Standard Specific to ENM?	0%
Section 9 Chem and Phys properties Dispersibility, particle size	0%
Section 11 Toxicology Specific information for ENM	0%
Section 12 Ecology Specific information for ENM	29% (2/7)

[a.] Reliability is a combination of relevance and accuracy. Relevance was rated between 1 (poor) to 5 (highly) and accuracy was rated between 1(inaccurate) and 3 (highly accurate). Refer Appendix 1 and Section 3.

5.5 Others

Of the twelve other MSDS evaluated, nine do not identify the engineered nanomaterial contained in the product. Thus it is not possible to comment on the adequacy or accuracy of the hazard identification presented within these MSDS. All the nine MSDS are for nanomaterials in solution, thus the likelihood of exposure may be reduced or increased depending on the application technique. For instance eight of the nine MSDS are for surface coating formulations that may be applied by aerosol (spray can or spray pack).

The remaining three are; boron nitride nanotubes, tricalcium phosphate hydrate, and “nanoclay” (MSDS #16, #23, #35).

The MSDS for boron nitride was very poor. Not only did it not comply with the Australian Code of Practice [NOHSC 2011(2003)] but it did not contain any pertinent information on the nanotubes, and it did not contain any statements about the lack of knowledge and need for caution as a consequence.

An MSDS for nano-sized calcium phosphate did not contain specific information on physicochemical properties although the particle size and other specifications are available on accompanying product literature. Nanoclay is described as non hazardous and the exposure standard for nuisance dust is provided.

Given the paucity of ENM specific information for these MSDS and a lack of knowledge on the nano-sized toxicity of these substances, it is difficult to conclude that the MSDS are adequate for hazard identification purposes.

6 Evaluation results for labels

Fifteen labels were evaluated, twelve from Australian suppliers, and fourteen of the substances were classified as hazardous substances. All labels were for containers of solutions containing engineered nanomaterials and most were intended for use in laboratories (reagent supplier labels). Table 6.1 summarises the label evaluation findings.

Table 6.1 Label Evaluation Criteria

Evaluation Criteria	% of labels that meet criterion
Does the label identify that the product contains a nanomaterial?	93% (14/15). Labels include the word “nano” within the product name or product description. Laboratory reagent labels (n=9) contain the word “nanopowder” in product description and particle size. For a label for carbon nanotubes the name “Synthetic graphite powder” is included. This is considered an inaccurate description for a carbon nanotube.
Does the label contain hazard statements?	93% 14/15. Nanoclay was classified as non hazardous. All classified as hazardous identified the hazard as irritation or flammability.
If an Australian supplier does the label comply with [NOHSC:2012(1994)].	100% (10/10[a]). Ten Australian product labels for hazardous substances were evaluated against the requirements of the Code of Practice and all comply.
Does the label advise on exposure control (dust or aerosol generation, ventilation)	Inclusion of a statement to avoid dust exposure/breathing dust and a statement on ventilation was found on all labels.

Key observations made for labels of products containing Engineered Nanomaterials (ENM):

- Practically all (14/15) labels included the word “nano” within the product name or product description. Laboratory reagent labels (n=9) contain the word “nanopowder” in product description and also the particle size.
- The labels accurately reflected the content as presented on the MSDS. Thus the inadequacies identified in relation to chemical identification and hazard classification in Sections 5 also apply to the labels. For instance on one label for carbon nanotubes the name was described as “Synthetic graphite powder”, an inaccurate description for a carbon nanotube.
- The labels did not contain additional cautionary notes regarding the suspected hazards of Engineered Nanomaterials (ENM). Although not mandatory a cautionary note warning users that the hazards of ENMs have not been fully elucidated and emphasising the need to handle with care would be useful and relevant information.

7 Discussion

The finding that most MSDS are based on bulk material properties (hazard classification, physicochemical properties, exposure standards and toxicity data) is consistent with previous surveys of MSDS by other organisations.

Conti et al. (2008), in an international survey of nanomaterials firms and laboratories, comment that the most common product stewardship advice available was MSDS for bulk materials.

Norden et al. (2007) conducted a survey of ENM MSDS retrieved (suppliers + internet) between June 2006 and January 2007. The following ENM MSDS were obtained; Silica (8), Titanium dioxide (4), Zirconium dioxide (2), Carbon nanotubes (11), C_{60} Fullerenes (2), Cadmium-based quantum dots (3). The findings were very similar to the findings outlined in Section 5. These include:

- Hazard classifications were not consistent with health effects section of the MSDS and very few toxicity test results were presented.
- In some cases “nano” was indicated in the commercial name of the material.
- The chemical name and/or CAS numbers on most carbon nanotube MSDS were identified as graphite.
  The quality of the proposed handling, storage and exposure controls/personal protection varied much between the MSDS even for materials of the same character. In some there was detailed recommendation on engineering controls and personal protection. For example, some MSDS recommended respiratory protection with specific (standard) filter types that are effective for protection against ultra-fine aerosols. In other MSDS the instructions for recommendations for handling, storage and exposure controls/personal protection were very brief.
- There was very little ecological information in the MSDS.

A very recent review by NIOSH of 60 MSDS from 33 different manufacturers of ENMs has been reported in a poster at a recent conference (NIOSH 2009b). Only 5% of MSDS were ranked as good with the remainder requiring “improvement” (40%) or “serious improvement” (55%).

Findings in common with the present assessment included:

- Carbon nanofibre MSDS commonly list occupational exposure limits (OELs) for graphite
- Most MSDS do not include a particle size distribution
- Most MSDS do not include toxicity data for ENM
- Many MSDS do not include specific information on ventilation or personal protective equipment.

A majority (9/15) of the labels evaluated were for laboratory reagents and thus intended for a professional audience. Practically all included a description of the material as “nano”.

Labels tend to include a short summary of key information that is presented in greater detail on the MSDS. Thus the inadequacies identified in relation to MSDS also apply to labels. The labels did not contain additional cautionary notes regarding the potential respiratory hazards associated with exposure to Engineered Nanomaterials (ENM).

8 Conclusions

The traditional information data sources for preparation of MSDS are unlikely to provide information on nanoparticles. Thus guidance is urgently needed on:

- Appropriate advice on search strategies to obtain relevant data (and frequency that such searches should be conducted)
- Interpretation of existing data for hazard identification purposes
- Hazard Classification for different types of ENMs
- Selection processes for appropriate exposure standards
- Appropriate cautionary statements for use on MSDS in the absence of data
- Specific recommendations for control measures particularly engineering controls and personal protective equipment for nano-sized particulates.

9 References

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Useful links on terminology

Definitions may be obtained from the following:

- ISO (2008a). Nanotechnologies - terminology and definitions for nano-objects - nanoparticle, nanofibre and nanoplate. International Organization for Standardization. ISO/TS 27687:2008

- 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/

Appendix 1 – Checklist for evaluation of MSDS

Date of evaluation:

MSDS Name:
MSDS Producer:

General overall comments.

Checklist
The following checklist was used during the evaluation of individual MSDS in order to provide a standardised record of the evaluation. The checklist and the instructions to evaluators are provided below.

1. Conformance to the Australian Code of Practice for Preparation of Materials Safety Data Sheets.

If the MSDS Address details are Australian non conformances to the Code of Practice need to be assessed in the following manner:

The evaluator needs to distinguish between mandatory requirement and a recommendation. When the requirement is met, a tick "✓" is entered. Non conformances are categorised as either "major" or "minor" depending on whether the item is a mandatory requirement or a recommendation.

For non hazardous substances the National Code of Practice is advisory only. Thus non conformances are categorised as "minor".

2. Relevance
An assessment of how relevant information in each section is to the engineered nanomaterial (i.e. representative of properties, hazards or controls). Either a descriptor of N/A (not applicable) or a rating of between 1-5 is entered (1 no relevance, 2 little relevance, 3 some relevance, 4 mainly relevant, 5 highly relevant).

3. Accuracy
Is assessed by considering the information presented and either; prior knowledge of a property, or inconsistencies for a property between different sections of the MSDS. For example, considering whether:

- the occupational exposure for nuisance dust is applied to a carbon nanotube
- first aid recommendations and toxicology data provided are inconsistent with hazard and risk phrases presented in Section 2.

Accuracy is assessed on a case by case basis. Accuracy is rated as 1= inaccurate, 2= partially accurate, 3= accurate. A comment is provided describing why the information is considered inaccurate or of limited accuracy.

4. Nano specific considerations

Relevance and accuracy ratings need to consider the reader is sufficiently informed about hazards to make their own judgement about potential hazards/controls for nanomaterials. Section 5 provides a discussion of important characteristics for ENMs considered during the evaluation of MSDS.

Date of evaluation:

MSDS Name: MSDS Producer:

General comments.

MSDS Section	Brief summary of ENM specific considerations (Section 5), refer to Table 2.1 for NOHSC requirements for each section.	Conformance [c] ✓ major, minor	Reliability	
			Relevance (N/A,1,2,3,4,5)	**Accuracy (1,2,3)**
Section 1 ID of the material and supplier	Product Name (does it specify nanoform) Recommended Use Supplier Name and Address, phone number(s) [a]		N/A	
Section 2 Hazards ID	Hazard classification [b] including a statement of overall hazardous or dangerous nature Risk and Safety phrase(s) Is it consistent with sections (8, 9, 10, 11, 12,14)?			
Section 3 Composition	Pure Substance (chemical name and CAS Number) Mixture (chemical name CAS Number and proportion of hazardous ingredients). Has the presence of a nano-object been identified in Section 3?			
Section 4 First Aid Measures	Description of necessary measures according to routes of exposure *Advice to medical staff*			
Section 5 Fire Fighting Measures	Extinguishing media, combustion hazards, precautions for fire fighters. Specific advice for easily oxidisable metallic			

MSDS Section	Brief summary of ENM specific considerations (Section 5), refer to Table 2.1 for NOHSC requirements for each section.	Conformance [c] ✓ major, minor	Reliability	
			Relevance (N/A,1,2,3,4,5)	Accuracy (1,2,3)
	dust?			
Section 6 Accidental Release Measures	Emergency procedure, methods and materials for containment and clean up.			
Section 7 Handling and Storage	Safe handling. Safe storage, incompatibility.			
Section 8 Exposure Controls / Personal Protection	National exposure standard, biological limit values, engineering controls, personal protective equipment.			
Section 9 Physical and Chemical Properties	Clearly identify the physical and chemical properties. Does it include properties useful for hazard identification? For listed ENM properties does it identify test method?			
Section 10 Stability and Reactivity	Chemical stability, Conditions to avoid, Incompatible materials, Hazardous decomposition products, Hazardous reactions.			
Section 11 Toxicology	Health effects information consistent with classification (Section 2) and first aid/medical advice?			
Section 12 Ecology	Ecotoxicity, persistence and biodegradability, mobility.			
Section 13 Disposal	Disposal methods, including disposal of container, Special precaution for landfill or incineration			
Section 14 Transport	UN Number, UN Proper Shipping Name, Class and subsidiary risk(s), Packing group, Special precaution of users, Hazchem Code			

MSDS Section	Brief summary of ENM specific considerations (Section 5), refer to Table 2.1 for NOHSC requirements for each section.	Conformance [c] ✓ major, minor	Reliability	
			Relevance (N/A,1,2,3,4,5)	Accuracy (1,2,3)
Section 15 Regulatory Information	Regulatory status of material under relevant Australian health, safety and environment legislation including: TGA Act, APVMA Act, ICNA Act.			
Section 16 Other	Date of preparation of MSDS, Data sources, Literature references, Key/legend of abbreviations and acronyms		N/A	

[a.] Only considered for MSDS obtained from companies based in Australia or MSDS with an Australian address.
[b.] Given the lack of current knowledge about the toxicity of nanomaterials and also due to the limited information on the characterisation and property testing of nanomaterials a classification of non hazardous should be consistent with data presented in the Material Safety Data Sheet. Titanium dioxide in the form of nano-size anatase and carbon nanotubes should be considered as hazardous unless toxicity data for the product show otherwise.
[c.] For non hazardous MSDS non-conformances were rated as minor given that the Code of Practice pertains only to hazardous substances.

Appendix 2 – MSDS obtained

MSDS Number (#)	Category
Metal oxide	
4	CdSe/ZnS
5	CdSe/ZnS
8	Zinc oxide
9	Alumina
10	Lead sulphide
11	Nano-silver
14	Aluminium oxide
15	“hybrid materials”
17	Titanium dioxide
19	Titanium dioxide
20	Titanium dioxide
21	Alumina
22	Zinc oxide
24	Nano – silver
32	Strontium ferrite
33	Tantalum, nanopowder
34	Yttrium oxide
Carbon nanotubes	
1	Carbon nanotubes (Fullerene, 99685-96-8),
6	Carbon nanotubes (Fullerene)
2	Carbon nanotubes (Graphite 7782-42-5)
3	Fullerene nanotubes
12	SWCNT
25	MWCNT
26	Carbon nanotubes (fullerene)
27	SWCNT
28	MWCNT
38	Carbon nanotubes
39	Carbon nanotubes
Silicates	
29	Silicon dioxide
30	Silicon nitride
31	Silicon carbide
36	3-aminopropyl (2-oxabutanoic acid) functionalized silica nanoparticles
37	Zirconium silicate
40	Silicon dioxide

MSDS Number (#)	Category
41	Silicon dioxide
Others	
7	Lanthanum nanoparticles
13	Gold nanoparticles
16	Boron nitride nanotubes
18	Not stated (5% composition "other")
23	Montmorillonite (containing crystalline silica as quartz)
35	Tricalcium phosphate hydrate
42	Not stated
43	Not stated
44	Not stated
45	Not stated
46	Not stated
47	Not stated
48	Not stated
49	Not stated