Department of Occupational Safety and Health
Ministry of Human Resources
Malaysia

GUIDELINE ON CONTROL AND SAFE HANDLING OF NANOMATERIALS 2018

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ISBN 978-983-2014-95-9

9 789832 014959

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PREFACE

The Guideline on Control and Safe Handling of Nanomaterials provide information and recommendations on handling of nanomaterials at workplace.

The application of nanotechnology in research or production processes may be exposed to nanomaterials through inhalation, skin contact/adsorption or ingestion. This guideline provides basic information to workers and employers on the current understanding of potential hazards associated with this rapidly-developing technology and highlights measures to control exposure to nanomaterials in the workplace.

Employers and workers must understand the rationale and importance of control and safe handling of nanomaterials at their workplace. This will minimise or help eliminate occupational illness due to hazards associated with the nanomaterials.

Industries are welcome to give any comment and recommendation to DOSH at any time so that improvements can be made to this guideline.

Director General
Department of Occupational Safety and Health
Malaysia
2018

ACKNOWLEDGEMENT

The Department of Occupational Safety and Health Malaysia (DOSH) wishes to thank and acknowledge the following individuals for their most valuable contributions during drafting of this guideline:

1. Shabanon binti Mohd Sharif
2. Hj. Jaafar bin Leman
3. Ir. Dr. Majahar bin Abd Rahman
4. Hj. Ghafar bin Kaprawi
5. Mohamad Hiswandy bin Ishak
6. Rusnah binti Nanyan
7. Mohammad Lui bin Juhari
8. Mohd Norhisyam bin Omar
9. Muhammad Faisal bin Jusoh
10. Noor Asriah binti Ramli
11. Noor Hafizie bin Sulkafle
12. Muhammad Shah bin Ab Rahim
13. Mohd Arif bin Mohd Nor
14. Azreen Shazwani binti Omar
15. Mohd Hafizullah bin Harun
16. Muhammad Azhar bin Tahrel
17. Syarikin binti Mat Nayah

1. PURPOSE

This guideline provides guidance and recommendation on safe handling and control of nanomaterials at workplace.

2. SCOPE AND APPLICATION

This guideline apply to use and handling of nanomaterials at workplaces specified under the scope of Occupational Safety and Health Act 1994.

3. INTRODUCTION

3.1 Nanomaterial

The key characteristic of a nanomaterial is that it presents properties that would not be found in the same materials at its normal scale.

Nanomaterial according to European Commission 2011 is a natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50 % or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm - 100 nm.

The International Organization for Standardization (ISO) defines a nanomaterial as a material with any external dimension in the nanoscale or having internal or surface structure in the nanoscale. The nanoscale is the size range from approximately 1 to 100nm, where an nm (nanometre) is a billionth of a metre, or in scientific terms, about 10 to the power of -9.

Size and example of nanomaterials in the environment are as in the Figure 1.

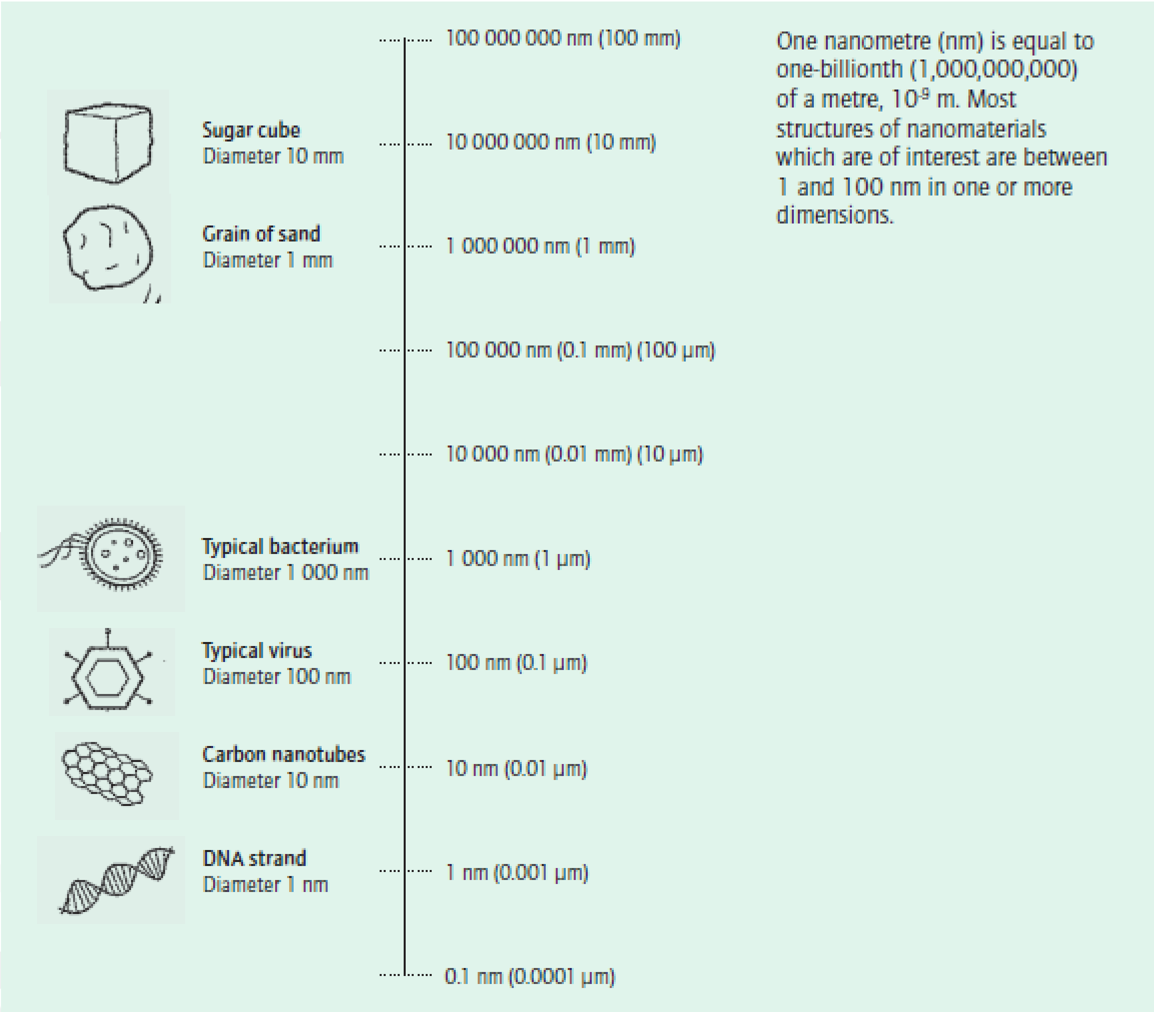


Figure 1 : Nanomaterials in the Environment (Royal Commission on Environmental Pollution, 2008)

3.2 Nanotechnology

Atoms and molecules are the essential building blocks of all things. The manner in which things are constructed with these building blocks is vitally important to their properties and how they interact. Nanotechnology is the manipulation of matter at the atomic scale to create materials, devices, or systems with new properties and/or functions. Around the world, the introduction of nanotechnology promises great societal benefits across many economic sectors: energy, healthcare, industry, communications, agriculture, consumer products, and others (Sellers et al., 2009). Consumer products which contain nanomaterials include acne lotions, antimicrobial treatment for socks, sunscreens, food supplements, components for computer hardware (such as processors and video cards), appliance components, coatings, and hockey sticks.

However, nanotechnology also presents new challenges for measuring, monitoring, managing, and minimizing contaminants in the workplace and the environment. The properties for which novel nanoscale materials are designed may generate new risks to workers, consumers, the public, and the environment. While some of these risks can be anticipated from experiences with other synthetic chemicals and with existing knowledge of ambient and manufactured fine particles, novel risks associated with new properties cannot be easily anticipated based on existing data.

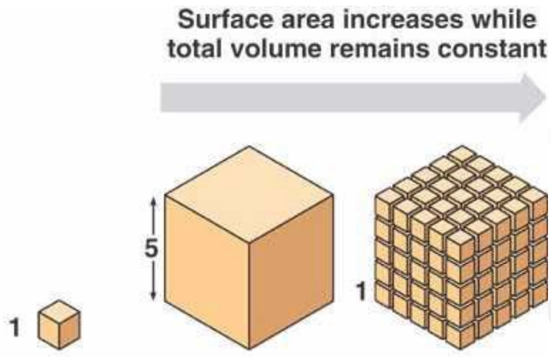
Nanotechnology is an emerging field. As such, there are many uncertainties as to whether the unique properties of engineered nanomaterials (which underpin their commercial and scientific potential) also pose occupational health risks. These uncertainties arise because of gaps in knowledge about the factors that are essential for predicting health risks-factors such as routes of exposure, translocation of materials once they enter the body, and interaction of the materials with the body’s biological systems.

The carbon nanotube is a unique nanomaterial being investigated for a wide range of applications. These tubes are cylinders constructed of rolled-up graphene sheets. Another interesting carbon structure is a fullerene (also known as a Bucky Ball). These are spherical particles usually constructed from 60 carbon atoms arranged as 20 hexagons and 12 pentagons. As shown in Figure 2, the structure resembles a geodesic dome (designed by architect Buckminster Fuller, hence the name). Nanomaterials are widely used across industries and products, and they may be present in many forms.

Figure 2 : **Atomic structure of a spherical fullerene**

3.2.1 Surface area to volume ratios in nanotechnology

The main focus of this paragraph is the interesting change in properties of materials due to increased surface area to volume ratio. Reactions take place at the surface of a chemical or material; the greater the surface for the same volume, the greater the reactivity. The link to nanotechnology is that as particles get smaller; their surface area to volume ratio increases dramatically as shown in Figure 3. Imagine a cube of sugar, reacting with water as the water dissolves the outside of the sugar. Now imagine the same cube of sugar cut into many little pieces. Each cut makes new outer surfaces for the water to dissolve. For smaller particles of sugar, the same volume of sugar now has much more surface area. A particle with a high surface area has a greater number of reaction sites than a particle with low surface area, and thus, results in higher chemical reactivity.



Total surface area (height × width × number of sides × number of boxes)	6	150	750
Total volume (height × width × length × number of boxes)	1	125	125
Surface-to-volume ratio (surface area / volume)	6	1.2	6

Figure 3 : Surface Area To Volume Ratio

Nanoparticles are special and interesting because their chemical and physical properties are different from their macro counterparts. The sugar example is interesting if you want to make tea sweet faster (use granules instead of cubes), but serves little real application. One prime example of surface area to volume ratio at the nanoscale is gold as a nanoparticle. At the macroscale, gold is an inert element, meaning it does not react with many chemicals, whereas at the nanoscale, gold nanoparticles become extremely reactive and can be used as catalysts to speed up reactions.

This increased reactivity for surface area to volume ratio is widely taken advantage of in nature, one biological example being the body's digestive system. Within the small intestine, there are millions of folds and subfolds that increase the surface area of the inner lining of the digestive tract. These folds allow more nutrients and chemicals to be absorbed at the same time, greatly increasing our body's efficiency and the rate at which we digest food.

3.3 Nanomaterials Applications in Malaysia

Nanomaterials have very wide applications in a lot of fields. Among such is the use of nanomaterials as fillers to produce lightweight and strong materials. Other than that, commercial uses of nanomaterials are blooming in cosmetics and medicinal product as the large surface area of nanomaterials used in the products can improve delivery and functionality of the product to the targeted areas.

In Malaysia, research and development on nanomaterials are actively being done by universities all over the country. Like all other developed countries, Malaysia is eager to take advantage of the potential of nanomaterials and venture into the world of commercialisation of the profitable novel materials.

Other than active participation in research and development by the universities, there are some industries which have ventured commercially in this field. Furthermore, Ministry of Science, Technology and Innovation (MOSTI) has established National Nanotechnology Centre (NNC) (formerly known as National Nanotechnology Directorate, NND) as the National Focal Point in order for the coordination of research, development and all related activities of nanotechnology.

4. PROCESS AND METHOD OF NANOTECHNOLOGY

Currently, nanomaterials are produced using a variety of methods that provide conditions for the formation of desired shapes, sizes, and chemical composition. These production processes can be separated into six categories (NIOSH, 2013).

4.1 Gas phase processes, including flame pyrolysis, high-temperature evaporation, and plasma synthesis

This process involves the growth of nanoparticles by homogenous nucleation of supersaturated vapour. Nanoparticles are formed in a reactor at high temperatures when source material in solid, liquid, or gaseous form is injected into the reactor. These precursors are supersaturated by expansion and cooled prior to the initiation of nucleated growth. The size and composition of the final materials depend on the materials used and process parameters.

4.2 Chemical vapour deposition (CVD)

This process has been used to deposit thin films of silicon on semiconductor wafers. The chemical vapour is formed in a reactor by pyrolysis, reduction, oxidation, and nitridation and deposited as a film with the nucleation of a few atoms that coalesce into a continuous film. This process has been used to produce many nanomaterials including titanium dioxide, zinc oxide, silicon carbide, and, possibly most importantly, CNTs. The use of fluidized bed technology has been adopted as a way to prepare CNTs on a large scale at low cost (Wang Y et al., 2002). This technology fluidizes CNT agglomerates and produces high yields necessary for larger-scale operations.

4.3 Colloidal or liquid phase methods

Chemical reactions in solvents lead to the formation of colloids. Solutions of different ions are mixed to produce insoluble precipitates. This method is a fairly simple and inexpensive way to produce nanoparticles and is often used for the synthesis of metals (e.g. gold, silver). These nanomaterials may remain in liquid suspension or may be processed into dry powder materials often by spray drying and collection through filtration.

4.4 Mechanical processes including grinding, milling, and alloying

These processes create nanomaterials by a “top-down” method that reduces the size of larger bulk materials through the application of energy to break materials into smaller and smaller particles. This technique has been referred to as nanosizing or ultrafine grinding.

4.5 Atomic and molecular beam epitaxy

Atomic layer epitaxy is the process of depositing monolayers (i.e., layers one molecule thick) of alternating materials and is commonly used in semiconductor fabrication. Molecular beam epitaxy is another process for depositing highly controlled crystalline layers onto a substrate.

4.6 Dip pen lithography

A “bottom-up” method is a production process that involves depositing a chemical on the surface of a substrate using the tip of an atomic force microscope (AFM). The AFM tips are coated with the chemical, which is directly deposited on a substrate in a specific pattern.

Downstream processes use engineered nanomaterials for product application and development. Examples of these tasks or operations include weighing, dispersion/sonication, mixing, compounding/extrusion, electro-spinning, packaging, and maintenance. These activities should be evaluated for potential sources of exposure.

5. SAFETY AND HEALTH CONCERNED

The question arises on whether nanomaterials would pose any safety and health risk to humans at large. The answer would be inconclusive. Research is still being done to determine the effect of nanomaterials on humans and the environment. No definite result can be obtained as for now.

However, DOSH as an agency that looks after the safety and health of workers, must be aware of the possibility of risks imposed on the workers by handling nanomaterials. Take for example, asbestos. The effect of the material on human health was never known during the early days of usage. Not until recent years, asbestos has been proven to cause cancer and efforts are being made to control the use of asbestos.

Nevertheless, it should be clear that the purpose of this document is not to hinder or stop altogether the emergence of nanomaterials in Malaysia, but it is merely to remind those involved in handling nanomaterials regarding the possible danger imposed by the nanomaterials and the importance of taking precautionary measurements when dealing with them. **Table 1** summarize the potential hazards according to the process or task involved:

Table1: Summarize of the Potential Hazards According to the Process/Task

PROCESS / TASK	WORK ACTIVITIES	DESCRIPTIONS	EXPOSURE TO NANOMATERIALS
Production of nanomaterials	Ball milling process	Use in powder metallurgy	Nanoparticles (dry powder) in the air
	Reactor fugitive emissions	Elevated concentrations of non-CNF ultrafine releases during thermal treatment of CNFs from the reactor	Nanoparticles in high concentration
	Product harvesting	Worker put his head into the hood to brush out the product powder	Nanoparticles in high concentration
	Reactor cleaning	Manual cleaning by sweeping and vacuuming to remove residual soot	Nanoparticles
Downstream processing	Product discharge / bag filling	The off-loading of product after spray drying	Airborne nanoparticles
		Powder product is commonly discharged into a bulk tote or drum before packaging	Nanoparticles (dry powder) in high concentration
	Bag / container emptying	Workers manually open and emptying bags of solid materials	Nanoparticles (dry powder) in high concentration
	Small-scale weighing	Handling of nanomaterials / nanoparticles during scooping, pouring and dumping activities	Nanoparticles in high concentration
	Machining of products	Machining of parts that containing nanomaterials (e.g sawing, polishing, grinding)	Nanoparticles
Product packaging	Small-scale weighing / handling	Handling of nanomaterials / nanoparticles for quality assurance/ control sample	Nanoparticles
	Large-scale weighing /	Large-scale powder packing, process loading	Nanoparticles in high concentration

PROCESS / TASK	WORK ACTIVITIES	DESCRIPTIONS	EXPOSURE TO NANOMATERIALS
Product packaging	handling	and tray dryer loading	
	Product packaging	Powder product is commonly discharged into a bulk tote or drum before packaging	Nanoparticles (dry powder) in high concentration
Maintenance	Facility equipment cleaning	When cleaning dust collection systems used to capture nanoparticles such as performing fan maintenance	Liquid or solid that contains nanomaterials
	Air filter change-out	Removal of dirty air filter from a ventilation unit	
	Spill clean-up	Cleaning up spills	Liquid or solid that contains nanomaterials

5.1 Identification of Hazard

The identification of hazards is the first step in determining risk and exposure. This step involves identifying nanomaterials, and their associated processes that pose health hazards (carcinogenicity, lung inflammation, etc.), physical hazards (e.g. high levels of noise, high pressures and vacuums, strong electromagnetic flux, etc.) and physicochemical hazards (reactivity, flammability, explosivity, etc.). In a comprehensive hazard identification process, all potential occupational hazards, including workplace chemicals should be identified in this step, including hazards that are low-level hazards or of low exposure potential, or hazards already being controlled in the workplace.

In order to identify hazards, information can be obtained generally from many sources including Safety Data Sheets (SDS), International Chemical Safety Cards (ICSC), publications from trade associations or government authorities, test data or proprietary information. For many nanomaterials there is currently a lack of specific knowledge of potential health effects, and exposure limits have not been established. Consequently these sources may not be able to provide sufficient information in order to adequately report the hazards associated with a specific engineered nanomaterial. The quality of information in some SDS has been reported as an issue, as has the lack of available SDS for some nanomaterials. If data are not available, then it may be possible to generate data through the testing of specific high-priority nanomaterials.

To understand and identify the hazards of the nanomaterials, the information about similar materials can be used. In this case, it is important to make sure that the information been used is truly applicable to the corresponding nanomaterial such as, carbon nanotubes (CNTs) and carbon nanofibres (CNF).

Many of the most commonly used nanomaterials have similar or the same chemical composition as larger scale particulates (often referred to as bulk materials). However, it is not clear which properties from a bulk material can be assumed to apply to a nano sized particulate.

In addition, the many differences between nanomaterials means that it is often not clear which properties of a nano sized particulate can be assumed to apply to other nano sized particulates. It is therefore important to consider 'sameness' when using information on one material to establish the hazardous properties of another material.

To determine the similarities and differences between different nanomaterials, it is important to obtain as much information as possible on the physical and chemical characteristics of each. It is suggested as a minimum that the following characteristics could be used to establish 'sameness':

- Chemical composition and purity
- Particle size distribution. Specialist advice from the supplier or an expert in the field of nano characterisation may be seek to make sure that the particle size distribution information is suitable for the current situation.
- Surface functionalization / treatment
- Shape
- Surface area

The greater the differences between the physical and chemical characteristics of one material and another, even though they may have the same chemical composition, the more likely it is that hazard data for one material will not provide a suitable basis to assess the hazards of another. It is therefore important to have information on the physical and chemical characteristics of the material been used, in order to identify materials with similar characteristics that may have similar hazards. If the hazard data cannot properly establish the identity and characteristics of the material that has been tested, it is unwise to assume that the results are applicable to the nanomaterial.

5.1.1 Physicochemical hazard

The field of nanotechnology is relatively new, and therefore little is known about the potential occupational safety hazards that may be associated with engineered nanomaterials. However, the information that is available about the properties of nanoparticles indicates that under given conditions, engineered nanomaterials may pose dust explosion hazard and be spontaneously flammable when exposed to air because of their large surface area and overall small size. Processes that generate engineered nanomaterials in the gas phase or use or produce nanomaterials as powders, slurries, suspensions, or solutions, are likely to release nanoparticles into the air and therefore create the greatest risk for fire and explosion. Currently, the primary safety concerns associated with nanomaterials in the workplace are fire and explosion.

Some nanomaterials are designed specifically to generate heat through the progression of reactions at the nanoscale; this too may present a fire hazard that is unique to engineered nanomaterials.

The ability of nanomaterials to become electrostatically charged during transport, handling, and processing introduces a unique explosion hazard when dealing specifically with nanopowders. Their tendency to charge has been found to drastically increase as particle surface area increases. As a result, their large surface area may become highly charged and become their own ignition source if the powder is dispersed in the air.

Nanoparticles and nanostructured porous materials have been used for many years as effective catalysts for increasing the rate of reactions or decreasing the necessary temperature for reactions to occur in liquids and gases. Depending on their composition and structure, some nanomaterials may initiate catalytic reactions and increase the fire and explosion potential that would not otherwise be anticipated from their chemical composition alone.

5.1.2 Health hazards

The toxicity of nanoparticles may be affected by different physicochemical properties, including size, shape, chemistry, surface properties, agglomeration, biopersistence, solubility, and charge, as well as effects from attached functional groups and crystalline structure. The greater surface-area-to-mass ratio of nanoparticles makes them generally more reactive than their macro sized counterparts. These properties are the same ones that make nanomaterials unique and valuable in manufacturing many products. Currently, the toxicity of many nanomaterials is unknown, but initial research indicates that there may be health concerns related to occupational exposures.

5.2 Safety and Health Effect

The potential health risk following exposure to a substance is generally associated with the magnitude and duration of the exposure, the persistence of the material in the body, the inherent toxicity of the material, and the susceptibility or health status of the person exposed. More data are needed on the health risks associated with exposure to engineered nanomaterials. Results of existing studies in animals and humans on exposure and response to ultrafine or other respirable particles provide a basis for preliminary estimates of the possible adverse health effects from exposures to similar engineered materials on a nanoscale. NIOSH has published Recommended Exposure Limits (REL) of three nanomaterials, namely ultrafine titanium dioxide (TiO_2) at 300 µg/m^3 (NIOSH, 2011) and carbon nanotubes (CNTs) plus carbon nanofibers (CNFs) at 1.0 µg/m^3 (NIOSH, 2013).

Experimental studies in rodents and cell cultures have shown that the toxicity of ultrafine or nanoparticles is greater than that of the same mass of larger particles of similar chemical composition (Oberdörster et al., 1992, 1994a,b; Lison et al., 1997; Tran et al., 1999, 2000; Brown et al., 2001; Duffin et al., 2002; Barlow et al. 2005). In addition to particle surface area, other particle characteristics may influence toxicity, including surface functionalisation or coatings, solubility, shape, and the ability to generate oxidant species and to adsorb biological proteins or bind to receptors (Duffin et al. 2002; Oberdörster et al. 2005a; Maynard and Kuempel 2005; Donaldson et al. 2006). More research is needed on the influence of particle properties on interactions with biological systems and the potential for adverse effects. International research strategies for evaluating the safety of nanomaterials are actively being developed through cooperative efforts (Thomas et al. 2006).

Exposure to nanomaterials may occur through inhalation, dermal contact, or ingestion depending on how personnel use and handle them. The full health effects of exposures to nanomaterials are not fully understood at this time. For example, a peer-reviewed toxicity study on CNTs indicated that the toxicity of nanoparticles depends on specific physiochemical and environmental factors and thus the toxic potential of each nanoparticle needs to be evaluated separately (Helland et al., 2007). Results of existing studies in animals or humans provide some basis for preliminary estimates of areas of concern (Stanford University, 2009). Studies to date have indicated:

- Increased toxicity of ultrafine particles or nanoparticles as compared to larger particles of similar composition. Chemical composition and other particle properties can also influence toxicity (Oberdörester et al., 1992, 1994a,b, 2005a; Lison et al., 1997; Tran et al., 1999, 2000; Brown et al., 2001; Duffin et al., 2002; Barlow et al. 2005; Maynard and Kuempel 2005; Donaldson et al. 2006).
- A greater proportion of inhaled nanoparticles will deposit in the respiratory tract as compared to larger particles (ICRP 1994; Jaques and Kim 2000; Daigle et al. 2003; Kim and Jaques 2004).
- Nanoparticles can cross cell membranes and interact with sub cellular structures where they have been shown to cause oxidative damage and impair function of cells in culture.
- Nanoparticles may be capable of penetrating healthy intact skin and translocating to other organ systems following penetration (Takenaka et at. 2001; Kreyling et al 2002; Oberdörester et al. 2002, 2004; Semmler et al. 2004; Geiser et al. 2005).
- Catalytic effects and fire or explosion are other hazards to consider (Pritchard 2004).

5.3 Nanomaterial Risk Assessment (NaRA)

Nanomaterial risk assessment means the process of evaluating the risk to safety and health arising from hazards at work. Risk is the determination of likelihood and severity of the credible accident or event sequences in order to determine magnitude and to priorities identified hazards. It can be done by qualitative, quantitative or semi quantitative method.

Risk can be presented in variety of ways to communicate the results of analysis to make decision on risk control. For risk analysis that uses likelihood and severity in qualitative method, presenting result in a risk matrix is a very effective way of communicating the distribution of the risk throughout a plant and area in a workplace. Risk can be calculated using the following formula:

Risk = Likelihood x Severity

Risk also been defined as a probability of over exposure and the consequences of the exposure. This is so because of potentially toxic chemical may cause death or serious health effect if the exposure is substantial. Therefore the risk equation can also be defined as:

Risk = Hazard x Exposure

Assessment of health risks arising from exposure to nanomaterials or other substances requires understanding of the intrinsic toxicity of the substance, the levels of exposure (by inhalation, by ingestion or through the skin) that may occur and any relationship between exposure and health effects.

Risk assessment for nanomaterials can be carried out by using control banding method. The following control banding method is based on the method outlined by the COSHH Essential and GoodNanoGuide that can be used to guide the industries on the matters pertaining to nanomaterials.

The example of methodologies being used for conducting risk assessment listed in Appendix 2 and 3.

5.3.1 Steps to conduct assessment

Steps to conduct NaRA is summarized as the following process flowchart:

Figure 4: NaRA Process Flowchart

Step 1: Gather information and identify material

Identify areas that have nanomaterials related activities. The areas involved should be specified for control banding purposes. Information of the material can be obtained, but not limited to these documents:

a) Chemical/Material register;
b) Safety Data Sheet (SDS) or other material information;
c) Label;
d) Information about the task where chemical/material is used and total duration of use;
e) Existing control measures such as general ventilation, local exhaust ventilation and etc;
f) Other information such as layout plan, process flow, operating temperature of process and number of workers exposed to chemical/material.

Step 2: Determine the degree of release

The potential for exposure is described through the state of the nanomaterial as shown in **Table 2**.

Table 2: State of the Nanomaterial

State of the nanomaterial	Description
Bound	• Nanoparticles in solid matrix. • Nanoparticle dispersed and fixed within a polymer matrix, incapable, as a practical matter, of becoming airborne.
Potential	• Nanoparticles in friable or sol gel matrix.
Free/Unbound	• Nanoparticles unbound, not aggregated, not contained within a matrix that would be expected to prevent the nanoparticles from being separately mobile and a potential source of exposure. • Particle suspended as an aerosol or in a liquid.

Step 3: Determine exposure duration

Exposure duration is categorised into short, medium and long based on duration of exposure to nanomaterials as specified in **Table 3**. Duration of exposure must consider work activities or processes involving exposure to nanomaterials.

Table 3: Exposure Duration

Category	Description
Short	< 4 hours/day, 2 days/week
Medium	4 to 6 hours/day, 3 to 5 days/week
Long	6 to >8 hours/day, 3 to 5 days/week

Step 4: Determine hazard group

Nanomaterials are grouped into three hazard groups:

Table 4: Hazard Group

Category	Description
A	Known to be inert
B	Understand reactivity and function
C	Unknown properties

Step 5: Determine control band (risk level)

Determine the risk level or control band using **Table 5**.

Table 5: Control Matrix

Degree of Release / Exposure Duration	Bound Materials	Potential Release	Free / Unbound
Hazard Group A (Known to be inert)			
Short	1	1	2
Medium	1	1	2
Long	1	2	2
Hazard Group B (Understand reactivity/function)			
Short	1	2	2
Medium	1	2	3
Long	1	3	3
Hazard Group C (Unknown properties)			
Short	2	2	3
Medium	2	3	4
Long	2	4	4

Control Band (Risk Level) Key

Band	Control Measures
1	General ventilation and personal protective equipment (PPE)
2	Engineering controls and/or respirators, additional PPE
3	Containment (e.g. glove box)
4	Seek specialist advice

Step 6: Develop and implement action plan

Employer should develop action plan to control the exposure of nanomaterials based on the control band obtained. Refer to paragraph 5.4 for further details.Take account of any safety hazards (refer to advice on the SDS or any related safety information), which may affect the required controls and their implementation.

Consider additional actions required to fully comply with other legislation requirements and other recommended control measures. For example nanomaterials which are chemicals hazardous to health in the workplace should be referred to Occupational Safety and Health (Use and Standards of Exposure to Chemicals Hazardous to Health) Regulations 2000.

The measures, procedures, and equipment necessary to control any accidental emission of chemical hazardous to health as a result of leakage, spillage, or process or equipment failure should also be considered.

The development and implementation of the action plan should include the participation of employees. Employer should check the effectiveness of the control measures periodically.

Step 7: Report writing and record keeping

Assessments done should be documented properly and maintained for future reference. They can either be in hard copies (for example bound reports) or electronic copies. All records should be stored and maintained in such a way that they are readily retrievable and protected against damage, deterioration or loss.

5.4 CONTROL MEASURES

The four approaches are:

1 – General Ventilation and Personal Protective Equipment (PPE)

A good standard of general ventilation and good working practices. PPE should only be used when all other reasonably practicable measures have been taken, but these have not, in themselves, achieved adequate control.

2 – Engineering Control and Respirators, Additional PPE

Typically, local exhaust ventilation ranging from a single point extract close to the source of hazards, to a ventilated partial enclosure. It includes other engineering methods of control, e.g. cooling coils for vapours, but not complete containment. When choosing respirators, it should be suitable and manufactured to an appropriate standard.

3 – Containment (e.g. glove box)

The hazard is contained or enclose, but small-scale breaches of containment may be acceptable. Often used where a substance is very hazardous or a lot of it is likely to get into the air.

4 – Seek specialist advice

Specialist advice is needed in selecting control measures and to seek further help.

Least reduction in exposure

↓

Greatest reduction in exposure

Special help needed

5.4.1 General ventilation

This control measures applied to assessment which results in Band 1. It is a control of the contaminants generated in a space by diluting it with uncontaminated outside air flowing into the room in large quantities so as to reduce the concentration of air contaminants to acceptable levels. There are two types of general or dilution ventilations, i.e. natural ventilation and forced ventilation.

Natural ventilation

- Produced by movement of air entering and leaving through the openings such as by opening of windows or doors to allow air to exchange naturally.
- Should not be used as control measures to reduce workers exposure in a workroom.

Forced ventilation

- There are three types of mechanically induced air movement used to dilute contaminant
    - i) supply system
    - ii) exhaust system
    - iii) supply-exhaust system

- Use of mechanical fan e.g. axial fan to move air out of space for the purpose of diluting the contaminants in the space.

Figure 5: Industrial axial fan

5.4.2 Engineering control

This control measures applied to assessment which results in Band 2. Methods of control that apply engineering principles such as local exhaust ventilation, cooling coil for vapours, water spray, etc. are also highly encouraged to eliminate or minimise the risk of exposure to nanomaterials.

Local Exhaust Ventilation (LEV) is a system that consists of hood, duct, air cleaner/filter, exhaust fan e.g. centrifugal fan and exhaust stack to capture or remove contaminant at/near source or point of release for example fume cupboard, spray booth, etc.

5.4.3 Containment

This control measures applied to assessment which results in Band 3. The hazard is contained or enclosed due to the very hazardous nature of the nanomaterials. It is a closed system with limited breach of containment.

5.4.4 Seek special advice

This control measures applied to assessment which results in Band 4. Seek special advice means a situation where more specific and specialist advice needed. The advice may come from an expert such as:

- qualified occupational hygienist;
- professional engineer; or
- subject matter expert of nanomaterials.

These experts can give site-specific advice on risk assessment, the possibility of substituting the nanomaterials for a less hazardous materials, and suitable control measures.

5.5 Personal protective equipment (PPE)

PPE is used to complement other control measures for added precaution. Protective equipment only protects the person wearing it, not anyone else. This also needs checking and maintenance because if it fails it no longer provides protection and exposes the wearer to the hazard. Users need to know exactly how to use and store their PPE correctly as do supervisors. Employer should train their workers on proper use of PPE. Selection of PPE should be done based on the possible routes of exposure of nanomaterials. For example, respiratory protection for inhalation, protective clothing for skin and eyes.

5.5.1 Protective clothing

Protective clothing is attire that covers the whole body such as lab coats, long pants and shoes should be worn to avoid incidental exposures of nanomaterials to skin. Non-woven materials are also preferred as the intertwined fibres can avoid nanomaterials penetration. Lab coats that are made out of non-woven materials are recommended to be worn when handling nanomaterials.

For some situations (low hazard material, low exposure risk), use of cotton or cotton-polyester lab coats or coveralls may provide sufficient protection.

For higher risk scenarios (high hazard material or high nanomaterials exposure potential), protective clothing should be made from a low dust-retention/low dust-release fabric. Nonwoven textiles (e.g. high-density/airtight polyethylene) can provide a high level of protection. Avoid protective clothing made of paper, wool, cotton, or other woven fabrics (e.g. polyester) for handling materials of high concern. Common types of protective clothing for powder handling include a lab coat, long sleeves without cuffs, long pants without cuffs, coveralls, closed-toe shoes made of low-permeability material, and shoe covers.

When a high level of protection is needed, consider using protective clothing with a hood. Interfaces between chemical protective clothing and respirator, protective footwear covering, and gloves can be sealed with tape to increase protection.

However, you must make provision for clean overalls/lab coats to be put on and dirty ones removed in a manner that does not contaminate individuals or the general workplace. If reusable lab coats or overalls are used you must consider their laundering and prevention of secondary exposure. (In the event of a 'one-off' gross contamination, consider treating even 'reusable' PPE as disposable.)

How often they need to be changed and laundered will depend on the type of task. As a minimum, it is suggested that lab coats should be changed at least once a month. Do not allow work wear to be taken home for laundering.

5.5.2 CNTs and other biopersistent High Aspect Ratio Nanomaterials (HARNs)

For CNTs and other biopersistent HARNs, protective clothing made of materials such as polyethylene textiles (eg Tyvek) performs better than a standard lab coat as this type of material does not retain dust or allow dust to penetrate, and can be disposable. Wool, cotton poly-cotton or knitted material, which can retain dust, is not recommended.

Nanomaterials can permeate through some intact disposable overall materials and by implication woven reusable materials (European Nanosafe). Non-woven Tyvek/Tychem polyethylene overalls are recommended for use with nanomaterials, rather than paper or cotton.

Figure 6: Tychem

Figure 7: Tyvec

5.5.3 Gloves

Use suitable disposable single-use gloves manufactured to an appropriate standard. Glove material thickness is a major issue in determining diffusion of nanomaterials and this should be considered in the risk assessment. If the risk assessment indicates latex is the safest choice, then only use low-protein powder-free gloves.

Other substances which may be involved during the nanomaterial handling process, e.g. solvents, must be considered in choosing gloves material. Employees should be properly trained in how to put on and remove gloves without contaminating themselves.

Figure 8: The incorrect (left) and the correct way (right) to wear glove (NIOSH UK, 2012)

5.5.4 Eye protection

Use of suitable eye protection is recommended when handling any chemicals, this includes all nanomaterials. A minimum of close fitting safety glasses should be used for all nanomaterials.

5.5.5 Respiratory protective equipment (RPE)

When choosing RPE it should be suitable and manufactured to an appropriate standard. Also consider any other chemicals, e.g. solvents, which may be used when handling nanomaterials. Check with RPE supplier for the most suitable filter.

When RPE is used as a secondary control for emergencies or accidental spillages or where additional protection is required as indicated by the risk assessment, disposable and half-masks should have an assigned protection factor (APF) of no less than 20.

When RPE is used as a primary control, i.e. the only method of control (not recommended unless no other method available), use a full-face with mask with APF 40, preferably powered if used for over one hour.

All types of masks (including disposable) must be suitable for the task and face-fitted for the individual by a competent face-fit tester. Employees should be properly trained in RPE use and supervised. If the equipment is reusable, it should be regularly cleaned and checked to ensure that it remains effective. Written records of RPE maintenance must be kept.

5.5.6 Other recommended control measures

5.5.6.1 Elimination

Elimination is definitely not a favourable option to be considered by the industries as nanomaterials are very lucrative products that can improve the quality of life. As long as there is no solid evidence of nanomaterials being harmful to humans and the environment, nanomaterials will continue to be developed, produced and used widely.

5.5.6.2 Substitution

Substitution on the other hand, can be applied to the process of producing nanomaterials. Different method and mechanical or chemical process can be opted for instead of using hazardous method or chemicals to produce nanomaterials.

5.5.6.3 Isolation

Isolation of processes involving nanomaterials are currently the most practiced form of control. Most of the equipment used for producing nanomaterials is made with built in isolation features. Other than that, the use of gloveboxes as isolation tools is also encouraged during handling of nanomaterials.

5.5.6.4 Administrative control

Other than that, the application of administrative control through the compliance to safe operating procedures (SOP) by all workers should also be implemented. An example of this is outlined in the Nanotoolkit developed by California Nanosafety Consortium of Higher Education. Although the Nanotoolkit is focused on academic research setting, the concept of developing an SOP for a specific task brought forward by Nanotoolkit can be adopted. Workers must also be given enough training to ensure correct handling, storage and disposal of the nanomaterials.

5.5.5.6 Cleaning spillages

All equipment used and the workplace must be thoroughly cleaned by using the wet-wipe method after each use of in case of spillage. It is prohibited to brush, use compressed air or standard vacuum cleaner for any cleaning purposes.

A dedicated commercial HEPA-filtered cleaner with the filter regularly changed can be used for cleaning purposes but caution should be taken especially when disposing of the used filter. The used filter should be treated as hazardous waste and disposed accordingly using precautionary approach.

Emergency procedures should be in place to deal with spills, accidents and emergencies.

5.5.6.6 Signage in the workplace for nanomaterials

Workplaces with nanomaterials should be posted with safety signs which indicates the use of nanomaterials at that area and usage of suitable PPE with the addition of any relevant and specific information on any actual or potential hazards of the specific nanomaterial handled.

Appropriate hazard labels, signs or pictograms should be selected based on the hazard information available regarding the material. Precautionary approach should be adopted if no specific information is available.

5.6 Remove, Reuse, Disposal of Nanomaterials

Waste nanomaterials classified as 'hazardous waste' must be disposed of in a safe and appropriate manner. For further information, please refer to specific requirement by relevant authorities (i.e. Department of Environment).

Procedures for removing PPE, including sequence and technique, should be tailored to the specific combination of PPE worn and level of PPE contamination to prevent exposing the worker or contaminating the work area. Used PPE should be removed carefully in the designated area. Workers wearing potentially contaminated PPE should avoid touching surfaces that will be touched by others not wearing PPE. The worker should avoid skin contact with contaminated PPE surfaces and avoid stretching and 'snapping' gloves or elastic cuffs/closures to prevent release of nanomaterials contamination into the air or onto other surfaces. When respirators are worn they should be removed after other outer PPE. An example sequence of PPE removal follows:

1. Remove disposable outer gloves. Allow first glove to turn inside out as it is being slowly removed; hold it in double-gloved hand then remove other hand's outer glove turning it inside out and pulling it over the first glove removed to contain it as if in a 'bag'. Discard into waste receptacle.
2. Remove goggles and place into cleaning receptacle, as needed.
3. Remove lab coat. If known to be contaminated, turn it inside out as it is removed, gently fold in on itself to keep contamination contained, and deposit into waste or laundry receptacle.
4. Remove respirator and place into waste or cleaning receptacle.
5. Remove inner gloves (as in #1 above), discard, and then wash hands and forearms.

For PPE (e.g. lab coats or coveralls) that will be reused, secondary exposure must be addressed prior to, and during, cleaning or laundering. A lab coat with no suspected or visible contamination that will be reused should be hung on an individual hook so the outside of one coat does not contaminate the inside of another. For disposable items, ensure that contaminated PPE is properly disposed. If gross contamination of reusable PPE occurs, consider disposal rather than cleaning. Secondary contamination from used PPE may be prevented (whether prior to laundering or disposal) by collecting items in an appropriately labelled plastic bag or other sealable container as they are removed. Workers should be educated on methods and practices to prevent them from inadvertently taking nanomaterials contamination home.

GLOSSARY

Terms	Definition
Nanofibre	A nanomaterial with two external dimensions at the nanoscale with a nanotube defined as a hollow nanofibre and a nanorod as a solid nanofibre
Nanoparticle	A nanomaterial with all three external dimensions at the nanoscale
Nanoaerosol	Nanomaterial may be suspended in a gas
Nanocomposite	Nanomaterial may be embedded in a matrix
Ultrafine particles	Nanometre diameter particles that have not been intentionally produced but are the incidental products of processes involving combustion, welding, or diesel engines
CNT	Carbon nanotubes
CNF	Carbon nanofibres

REFERENCES

1. Ajayan P. M. and Zhou O. Z. (2001) Applications of carbon nanotubes, Topics in Applied Physics, 80, 391-425
2. Barlow PG, Clouter-Baker AC, Donaldson K, MacCallum J, Stone V [2005]. Carbon black nanoparticles induce type II epithelial cells to release chemotaxins for alveolar macrophages. Particle and Fiber Toxicol 2, 14 pp [open access].
3. Brown DM, Wilson MR, MacNee W, Stone V, Donaldson K [2001]. Size-dependent proinflammatory effects of ultrafine polystyrene particles: A role for surface area and oxidative stress in the enhanced activity of ultrafines. Toxicology and Applied Pharmacology 175(3): 191-199.
4. Daigle CC, Chalupa DC, Gibb FRMorrow PE, Oberdorster G, Utell MJ, Frampton MW [2003]. Ultrafine particle deposition in humans during rest and exercise. Inhalation Toxicol 15(6):539–552.
5. Donaldson K, Aitken R, Tran L, Stone V, Duffin R, Forrest G, Alexander A. [2006] Carbon Nanotubes: a Review of Their Properties in Relation to Pulmonary Toxicology and Workplace Safety. Toxicol Sci. 92(1): 5-22.
6. Donaldson K. et al. (2006) Carbon nanotubes: a review of their properties in relation to pulmonary toxicology and workplace safety, Toxicological Sciences, 92 (1), 5-22
7. Duffin R, Tran CL, Clouter A, Brown DM, MacNee W, Stone V, Donaldson K [2002]. The importance of surface area and specific reactivity in the acute pulmonary inflammatory response to particles. Ann Occup Hyg 46:242–245.
8. EPA (Environmental Protection Agency) (2011) Pesticide news story: EPA announces conditional registration of nanosilver pesticide product, Press Release, 1 December 2011. http://www.epa.gov/oppfead1/cb/csb_page/updates/2011/nanosilver.html
9. Geiser M, Rothen-Rutishauser B, Kapp N, Schurch S, Kreyling W, Schulz H, Semmler M, Im Hof V, Heyder J, Gehr P [2005]. Ultrafine particles cross cellular membranes by nonphagocytic mechanisms in lungs and in cultured cells. Environ Health Perspectives 113(11):1555-1560.
10. Hagen Mikkelsen S. et al. (2011) Survey on basic knowledge about exposure and potential environmental and health risks for selected nanomaterials, Copenhagen, Danish Ministry of Environment, Environmental Project No 1370
11. Helland A, Wick P, Koehler A, Schmid K, Som C [2007]. Reviewing the Environmental and Human Health Knowledge Base of Carbon Nanotubes. Environ Health Perspectives 115(8):1125-1131.
12. ICRP [1994]. Human respiratory tract model for radiological protection. Oxford, England: Pergamon, Elsevier Science Ltd., International Commission on Radiological Protection Publication No. 66.
13. Jaques PA, Kim CS [2000]. Measurement of total lung deposition of inhaled ultrafine particles in healthy men and women. Inhal Toxicol 12(8):715–731.
14. Kim CS, Jaques PA [2004]. Analysis of total respiratory deposition of inhaled ultrafine particles in adult subjects at various breathing patterns. Aerosol Sci Technol 38:525-540.
15. Kreyling WG, Semmler M, Erbe F, Mayer P, Takenaka S, Schulz H, Oberdorster G, Ziesenis A [2002]. Translocation of ultrafine insoluble iridium particles from lung epithelium to extrapulmonary organs is size dependent but very low. J Toxicol Environ Health 65(20):1513–1530.

16. Lison, D., C. Lardot, F. Huaux, G. Zanetti, Fubini B [1997]. Influence of particle surface area on the toxicity of insoluble manganese dioxide dusts. Arch. Toxicol. 71(12): 725-729.
17. Maynard AM, Kuempel ED [2005]. Airborne nanostructured particles and occupational health. J Nanoparticle Research 7(6):587-614.
18. NIOSH [2009]. Approaches to Safe Nanotechnology: Managing the Health and Safety Concerns Associated with Engineered Nanomaterials, http://www.cdc.gov/niosh/docs/2009-125/
19. NIOSH (National Institute for Occupational Safety and Health) (2010) Occupational exposure to carbon nanotubes and nanofibres, Current Intelligence Bulletin
20. NIOSH [2013]. Current Strategies for Engineering Controls in Nanomaterial Production and Downsteam Handling Processes, DHHD (NIOSH), US, pp. 3-21.
21. Nowack B. et al. (2011) 120 Years of nanosilver history: implications for policy makers, Environmental Science & Technology, 45 (4), 1177-1183
22. Oberdörster G, Ferin J, Gelein R, Soderholm SC, Finkelstein J [1992]. Role of the alveolar macrophage in lung injury—studies with ultrafine particles. Environ Health Perspect 97:193–199.
23. Oberdörster G, Ferin J, Lehnert BE [1994a]. Correlation between particle-size, in-vivo particle persistence, and lung injury. Environ Health Perspect 102(S5):173–179. Oberdörster G, Ferin J, Soderholm S Gelein R, Cox C, Baggs R, Morrow PE [1994b]. Increased pulmonary toxicity of inhaled ultrafine particles: due to lung overload alone? Ann. Occup. Hyg. 38(Suppl. 1): 295-302.
24. Oberdörster G, Sharp Z, Atudorei V, Elder A, Gelein R, Lunts A, Kreyling W, Cox C [2002]. Extrapulmonary translocation of ultrafine carbon particles following whole-body inhalation exposure of rats. J Toxicol Environ Health 65 Part A(20):1531–1543.
25. Oberdörster G, Oberdörster E, Oberdörster J [2005a]. Nanotoxicology: an emerging discipline evolving from studies of ultrafine particles. Environ Health Perspect. 113(7):823–839.
26. Ponce Del Castillo, A.M. (2013) Nanomaterials and Workplace Health & Safety. What are the Issues for Workers? European Trade Union Institute.
27. Pritchard DK [2004]. Literature review—explosion hazards associated with nanopowders. United Kingdom: Health and Safety Laboratory, HSL/2004/12.
28. Royal Commission on Environmental Pollution [2008]. Novel Materials in the Environment: The case of nanotechnology, Twenty–seventh Report edn., London, pp. 11.
29. Sakamoto Y. et al. (2009) Induction of mesothelioma by a single intrascrotal administration of muti-walled carbon nanotube in intract male Fischer 344 rats, Journal of the Toxicological Sciences, 34 (1), 65-76.
30. SCENIHR (Scientific Committee on Emerging and Newly-Identified Health Risks) (2010) Opinion of the scientific basis for the definition of the term 'nanomaterial'. http://ec.europa.eu/health/scientific_committees/emerging/docs/scenihr_o_032.pdf.
31. Schinwald A. et al. (2012) The threshold length for fiber-induced acute pleural inflammantion: shedding light on the early events in asbestos-induced mesothelioma, Toxicological Sciences, 128 (2), 461-470.
32. Sellers K, Mackay C, Bergeson LL, Clough SR, Hoyt M, Chen J, Henry K, Hamblen J. [2009]. Nanotechnology and the Environment. Boca Raton, FL: CRC Press, pp. 296.

33. Semmler M, Seitz J, Erbe F, Mayer P, Heyder J, Oberdorster G, Kreyling WG [2004]. Long-term clearance kinetics of inhaled ultrafine insoluble iridium particles from the rat lung, including transient translocation into secondary organs. Inhal Toxicol 16(6-7): 453-459.
34. Sinha N. and Yeow J.T.W. (2005) Carbon nanotubes for biomedical applications, IEEE Transactions on Nanobioscience, 4 (2), 180-195
35. Stanford University [2009]. General Principles and Practices for Working Safely with Engineered Nanomaterials, https://web.stanford.edu/dept/EHS/prod/researchlab/IH/nano/docs/Working_Safely_with_Engineered_Nanomaterials.pdf
36. Takagi A. et al. (2008) Induction of mesothelioma in p53+/mouse by intraperitoneal application of multi-wall carbon nanotube, Journal of Toxicological Sciences, 33 (1), 105-116.
37. Takenaka S, Karg D, Roth C, Schulz H, Ziesenis A, Heinzmann U, Chramel P, Heyder J [2001]. Pulmonary and systemic distribution of inhaled ultrafine silver particles in rats. Environ Health Perspect 109(suppl. 4):547-551.
38. Tran CL, Cullen RT, Buchanan D, Jones AD, Miller BG, Searl A, Davis JMG, Donaldson K [1999]. Investigation and prediction of pulmonary responses to dust. Part II. In: Investigations into the pulmonary effects of low toxicity dusts. Contract Research Report 216/1999 Suffolk, UK: Health and Safety Executive.
39. Wang Y, Wei F, Luo G, Yu H, Gu G [2002].The large-scale production of carbon nanotubes in a nano-agglomerate fluidized-bed reactor, Chem Phys Lett 364(5–6):568–572.
40. Wijnhoven S.W.P. et al. (2009) Nano-silver: a review of available data and knowledge gaps in human and environmental risk assessment, Nanotoxicology, 3 (2), 109-138
41. www.bag.admin.ch/nanotechnologie/12171/12174/12175/index.html?lang=en
42. www.nanoriskframework.com
43. www.aist-riss.jp/main/modules/product/nano_rad.html?ml_lang=en
44. www.bmu.de/en/service/publications/downloads/details/artikel/responsible-use-of-nanotechnologies-1
45. www.umweltrat.de/SharedDocs/Downloads/EN/02_Special_Reports/2011_09_Precautionary_Strategies_for_managing_Nanomaterials_KFE.pdf?__blob=publicationFile
46. www.safenano.org
47. http://www2.mst.dk/udgiv/publications/2011/12/978-87-92779-11-3.pdf
48. http://ec.europa.eu/environment/chemicals/nanotech/reach-clp/ripon_en.htm
49. http://www.safeworkaustralia.gov.au/sites/swa/about/publications/pages/at201008workhealthandsafetyassessmenttool
50. http://nano.stoffenmanager.nl
51. http://www.ibar.dk
52. http://nanoparticlelibrary.net/

APPENDIX 1

Common examples of nanomaterials at the workplace

a) Silicon dioxide, SiO_2

Nanomaterials like silicon dioxide or 'silica' are produced in high volumes and are extensively used in a variety of applications and products. Silica in bulk form has been widely used as a food additive for many years to clarify beverages, control viscosity and as an anti-foaming agent and dough modifier.

Silica can be also found in the nano form in some food products as an anti-caking agent (to prevent the formation of lumps), in the construction industry in high-performance concrete mixtures to increase concrete cohesion and reduce the tendency to particle segregation; and in paints and coatings. Nanosilica is being developed for biomedical applications such as cancer therapy, and drug delivery and in health care products.

Hydrophobic surfaces incorporating nano-silica. In nature, water is repelled by the rough surface of lotus leaves. The Lotus-effect™ has been patented by German scientist Dr Wilhelm Barthlott and refers to the idea of constructing surfaces with microscopic raised areas to make them self-cleaning; as a result, dirt and liquids cannot get into the surface and are repelled. Paints and coatings can incorporate silica particles making surfaces self-clean, anti-dirt, anti-graffiti or anti-fingerprint, with high durability. The same water-repellent, stay-clean property can be found in textiles, where fibres treated with the coating work in the same way to repel wet and dirt from the fabric.

b) Nanosilver

Different silver compounds are known to have been used for many years: colloidal silver, for example, has been widely used for medicinal and hygienic purposes to treat bacterial infections (Nowack, 2011).

Silver in the nano form is being manufactured and used in different products and applications to enhance efficiency. Nanosilver inhibits multiplication and growth of bacteria and fungi which cause infection, odour, itchiness and sores, and therefore has been used as an antibacterial, antifungal, anti-viral and anti-inflammatory agent. But it presents different toxicity to its bulk counterpart.

Nanosilver is currently found in different products: as a lining in plastic food containers, in underwear, sportswear or socks to kill bacteria, in toothbrushes, surface cleaners, lotions, toys; household appliances like dishwashers, vacuum cleaners and refrigerators. In electronics, nanosilver is mainly used in solder for circuit connections, while silver nanowires are used as nanoconnectors and nanoelectrodes for nanoelectronic devices. It also has medical uses in wound dressings, medical textiles and sterilization materials. Also, at the nanoscale, silver has unique optical and physical properties of potential value in medical diagnostics, drug delivery and imaging.

Industry advocates in the United States argue that nanoscale silver has been widely used in the market for at least 12 decades as colloidal nanosilver algaecides and composite materials. However silver formulations can vary in the size, solubility and aggregation of nanoparticles, meaning that there is no one single form of nanosilver (Wijnhoven 2009).

As far as human exposure goes, a Danish report (Hagen Mikkelsen 2011) has found no quantitative data on occupational and consumer dermal exposure. The report believes that consumers especially may be exposed to nanosilver due to its relatively widespread use in clothes, and exposure is also suspected to be highest in the working environment. The main exposure routes for occupational settings are inhalation and skin contact, but further data on exposure and human toxicity are needed. However studies from Armitage et al., 1996 and Lee et al., 2012 indicate that occupational exposures during nanosilver production and handling may result in significant inhalation exposures that are reflected by increases in blood silver levels. As regards the environment, there is scientific evidence that nanosilver is toxic to aquatic and terrestrial organisms (Wijnhoven 2009, EPA 2010). Certainly, more research is needed on the bonds between nanosilver and the product it is incorporated in, and whether changes occur in the chemical properties.

Nanosilver has latterly come under scrutiny from regulators, with the United States Environmental Protection Agency (EPA) deciding to look closely into it. In October 2011, the EPA published a notice that it was conditionally registering a pesticide product containing nanosilver as a new active ingredient. The product is used as a preservative for textiles. As a condition of registration, EPA is requiring additional data on the product that confirms that it will not cause unreasonable adverse effects on human health or the environment (EPA 2011).

In December 2011, the European Commission asked the Scientific Committee on Emerging and Newly Identified Health Risk (SCENIHR) to prepare a scientific opinion for 2013 assessing whether the use of nanosilver, in particular in medical care and in consumer products, could result in additional risks compared to more traditional uses of silver, and to assess whether the use of nanosilver to control bacterial growth could result in resistance of micro-organisms.

c) Multiwalled carbon nanotubes

Carbon nanotubes are a new form of carbon where nanotechnology development has brought a ferment of fabrication and commercialization activity since 1991. There are different types of nanotubes: single-walled (SWNTs) double-walled (DWCNTs) and multiwalled (MWNTs), differing in the arrangement of their graphene cylinders. SWNTs have only a single layer of graphene cylinders; DWCNTs have two layers, and MWNTs have many layers (Sinha and Yeow 2005). The ISO defines multiwalled carbon nanotubes (MWCNTs) as carbon nanotubes composed of nested, concentric or near-concentric graphene sheets with interlayer distances similar to those of graphite.

Their nano size, structure and topology give them unique mechanical properties like high stability, strength and stiffness, as well as special surface properties. In sum, they are stronger than steel but very light, offering much scope for practical applications, including the fabrication of reinforced fibres and nanocomposites, diverse uses for energy storage, spacecraft structures, and land and sea vehicles. They are also used in sports articles like tennis rackets, baseball bats, bicycle frames, skis and surfboards.

Some types of MWCNT present great mechanical strength and heat-dissipation properties, conducting electricity much better than copper, and so are finding extensive applications in the electronics and computer industries. In the biomedical sector they have applications in radiotherapy, for sensors, as carriers for drug delivery and for implantable nanosensors and nanorobots.

Probably the most on-trend and most marketed nanotechnology products are the MWCNTs. These are long, straight, multi-walled structures and regarded as “the most perfect fibre that has ever been fabricated” (Ajayan and Zhou 2001). Nevertheless, they have also shown adverse effects in animals, causing inflammation when deposited in the lungs and inducing asbestos-like effects. Scientists have, for example, reported that laboratory rodents when exposed to MWCNT develop mesothelioma (Poland 2008, Sakamoto 2009, Tagaki 2008).

According to Ken Donaldson, a toxicologist at the University of Edinburgh specialized in workplace health, long fibres compared to short fibres have greater potency of pro-inflammatory and genotoxicity activity (Schinwald 2012). Since CNTs have specific properties related to strength and durability, they can be translated into biopersistence in the human body. The retention of long fibres in the parietal pleura initiates inflammation. Since fibres cannot be removed from the lung, the lesion aggravates and may give rise to mesothelioma. MWCNTs may be pathogenic because they are (Donaldson 2006):

— Thin enough to get past the upper airways and into the areas of the lungs where oxygen diffuses into the bloodstream;

— Long enough to start harming the lungs because they break down natural defences found in the lungs;

— Durable in that they stick around for a long time without dissolving or being broken down by the body (biopersistence).

Those characteristics – length, diameter, biopersistence - are known as the fibre paradigm.

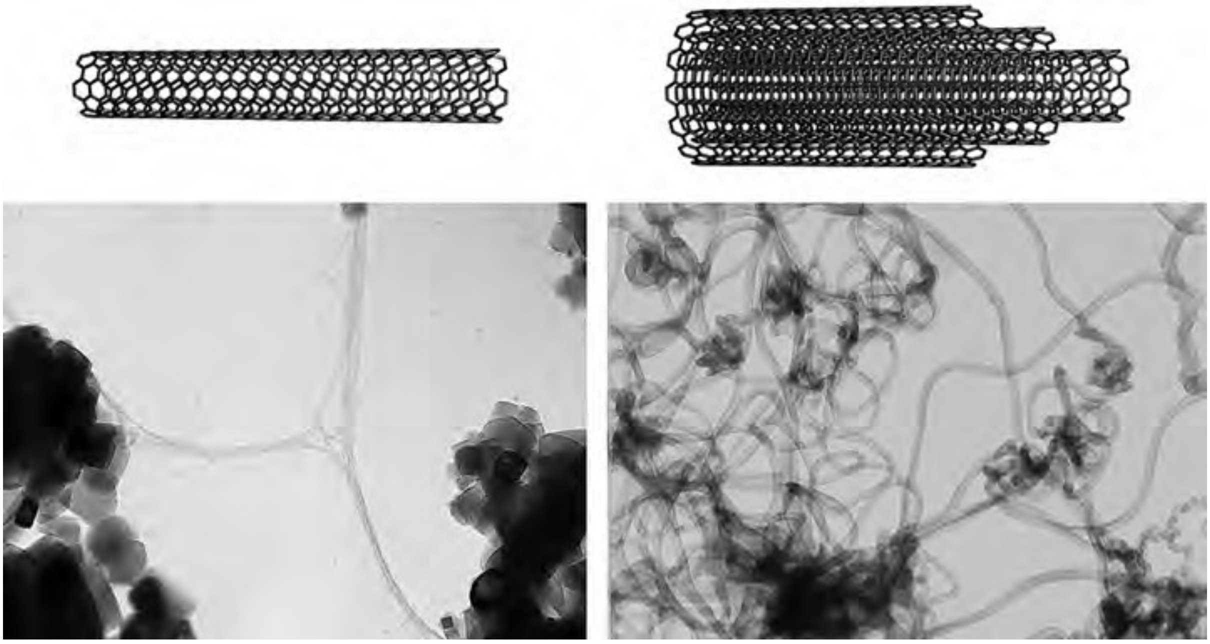


Figure 9: Single-Walled and Multi-Walled Carbon Nanotubes (Petrica Cristea 2013, Donaldson 2006)

MWCNT can be fabricated by different methods and processing conditions, so special care must be taken at the workplace. The US National Institute of Occupational Health and Safety has determined that workers may be at risk of developing adverse respiratory health effects if exposed for a working lifetime at upper limits according to their own methods for measurement of airborne CNTs (NIOSH 2010).

Workers' safety and protection must have top priority when dealing with this material. It is crucial for workers to be given sufficient enough information on the main processes they might possibly be exposed to (synthesis, collection, handling, purification and packing). While there is yet no scientific consensus on the dose and time needed to cause adverse health effects, workers should not be exposed to airborne MWCNT in any circumstances.

APPENDIX 2 – COMPARISON TABLE OF RISK ASSESSMENT

Overview on Current Nanomaterial Specific Risk Assessment Methodologies

Nanomaterial Specific Risk Assessment Methodology	Organization	Country	Description
Precautionary Matrix for Synthetic Nanomaterials	Federal Offices of Public Health and Environment (FOPH &FOEN)	CH	This tool allows the identification of potential risks for existing or new nanotechnology products and processes in the development, production, use and disposal stages by means of a methodical procedure. The potential risk of the nanomaterial or its associated products can be classified according to whether the requirement for nanospecific measures is estimated as low, or whether measures should be taken such as the evaluation of the current procedures, additional specifications, and, if necessary, practice measures to decrease the risks.
Nano Risk Framework	DuPont & Environmental Defense	US	This framework is established with the aim of providing assistance for the essential issues which should be taken into account when dealing with nanomaterials as well as offering support on the information required for performing risk evaluation and risk management decisions. The use of logical suppositions and suitable risk management procedures allow it to be adaptable enough to be applied in situations in which there is lack of knowledge or uncertainties. On the other hand, it offers the possibility of being used as a reference point when new developments take place or suppositions are made at the moment that new data is accessible. It is designed to be used iteratively as new data are generated and new information is gathered and includes a list of test methods for toxicity, ecotoxicity and environmental fate.
Risk Assessment of manufactured nanomaterials	New Energy and Industrial Technology Development	JP	This risk assessment methodology has been developed for three selected manufactured nanomaterials: TiO_2, fullerenes C60 and

Nanomaterial Specific Risk Assessment Methodology	Organization	Country	Description
	Organization (NEDO)		carbon nanotubes. The original concept had to be modified because a general chemical risk assessment was difficult to apply for nanomaterials. The reason for this is that the nanomaterials risk is influenced by the relationship between toxicity and physical properties rather than chemical properties alone. An additional difficulty encountered was the scarcity of toxicity and exposure data of the selected nanomaterials. The features taken into account are: the possibilities of functionalization of nanomaterials resulting in new biological reactions, small size or large specific surface area which allow nanoparticles to enter internal organs or may increase the activity of chemical reactions, persistence of nanoparticles and effect of shape on biopersistance.
NanoCommission Assessment Tool	Federal Ministry for the Environment, Nature Conservation & Nuclear Safety	DE	This methodology is based on the knowledge gained with the Precautionary Matrix for Synthetic Nanomaterials. This assessment tool is in the format of a downloadable questionnaire (available only in German). The set of criteria applied to all life-cycle stages are possibility of exposure, physico-chemical properties, environmental fate and toxicology/ecotoxicology. Beneficial and risk aspects of nanomaterials are considered for consumers, society, environment and companies at different stages of the life-cycle of a nanomaterial. A classification into two groups is made depending on whether there is no cause or cause for concern. Cause for concern arises when there is a risk of exposure due to high production and use volumes, high mobility of the nanomaterial, bioaccumulation, hazardous effects such as high reactivity, difficulties in risk management, i.e. due to low detectability and uncertainties in the fate of the nanomaterial.

Nanomaterial Specific Risk Assessment Methodology	Organization	Country	Description
Precautionary Strategies for Managing Nanomaterials	Advisory Council on the Environment	DE	This strategy describes the following actions which are proposed to improve the application of the precautionary principle to nanomaterials: increase on nanomaterial risk research; specific legal framework for nanomaterials; labelling and product register; review of chemical legislation; review of product legislation; review of environmental legislation and social dialogue. It is advised to consider nanomaterials as substances by themselves instead of as their conventional equivalents because nanomaterials can show additional risks than the bulk form. A basic data set for each nanomaterial, independently of the quantity produced, needs to be provided. Attention should be paid to waste incineration, landfilling, recovery and recycling, where waste containing nanomaterials should be sorted as hazardous.
SafeNano Scientific Services	Institute of Occupational Medicine (IOM)	GB	This commercially available service provides independent consultancy on nanomaterials risk and safety. It offers solutionson the following areas: Product safety and toxicology, nanoparticle detection and analysis, and duty of care and risk assessment. It helps to comply withregulatory requirements and provides support by means of safety procedures and toxicity testing. It offers expertise in determiningpossible nanoparticle exposure due to particle release in the workplace. The approach consists of obtaining the data needed for risk management due to problems arising throughout the supply chain. The areas covered include toxicology, hazard identification, eco toxicology, hazard assessment on ecological systems and bioaccumulation, safety issues and legislation, occupational hygiene and training for workers on nanomaterial safety and exposure risks.

Nanomaterial Specific Risk Assessment Methodology	Organization	Country	Description
NanoRiskCat – A Conceptual Decision Support Tool for Nanomaterials	Danish Ministry of the Environment – Environmental Protection Agency	GK	Through this project, DTU Environment and the National Research Centre for the Working Environment have initiated the development of a screening tool, NanoRiskCat (NRC), that is able to identify, categorize and rank exposures and effects of nanomaterials used in consumer products based on data available in the peer-reviewed scientific literature and other regulatory relevant sources of information and data. The primary focus was on nanomaterials relevant for professional end-users and consumers as, as well as nanomaterials released into the environment. The wider goal of NanoRiskCat is to help manufacturers, down-stream end-users, regulators and other stakeholders to evaluate, rank and communicate the potential for exposure and effects through a tiered approach in which the specific applications of a given nanomaterial are evaluated. This is done by providing detailed guidance on mapping and reporting.
REACH Implementation Projects on Nanomaterials (RIPoN)	European Chemicals Agency	EU	The European REACH legislation does not specifically mention nanomaterials although it comprises areas where nanomaterials are used and therefore it can be applied. Nanomaterials are deemed equivalent to their analogues in the bulk form for the purposes of registration In the case that the bulk and the nano form have different uses and properties, these must be specified and additional information, such as hazardous properties, operational conditions, safety assessment and risk management, needs to be provided. The particular hazards related to thespecific nanomaterials need to be tackled and therefore the test guidelines may need to be adjusted accordingly and further testing may be necessary.

Nanomaterial Specific Risk Assessment Methodology	Organization	Country	Description
Work Health & Safety Assessment Tool for Handling Engineered Nanomaterials	Safe Work	AU	This tool was developed to assist regulators, research laboratories and organizations in managing engineered nanomaterials. It consists of a questionnaire which helps to register the chemical composition and the physical form of the nanomaterials manufactured, used, and the safety measures applied to nanoparticle exposure prevention at the work place. Consumer protection or environmental considerations are not taken into account.
StoffenmanagerNano Module	Ministry of Social Affairs and Employment	NL	This web-based application focuses on the safety at the work place when dealing with not biodegradable engineered nanomaterials. The classification of the risk is made according to the physico-chemical characteristics and hazard properties of the nanomaterial. At the moment only a qualitative output can be obtained, which classifies the risk priority in low, medium or high. It evaluates the exposure to nanomaterials only via inhalation.
NanoSafer	The Industries Council of Occupational Health and Safety	DK	A risk evaluation methodology for the work place is described which takes as a reference the known hazards of the analogue bulk material and it only considers nanopowders. It employs a control banding method to estimate the hazard and exposure to airborne nanoparticles in the work place. Only a Danish version is available.
ANSES	National Agency for Food Safety, Environment and Labor	FR	A control banding approach is applied for the work place, combining risk assessment and management. It allows the use of data on toxicity of the similar conventional chemicals. Solubilityand reactivity are considered as factors increasing the hazard. Biopersistent fiber-like shape substances are considered to be of maximum hazard. It is requested to report the amount produced, the uses of the nanomaterial, the frequency of exposure and the final users