European Commission

# Working Safely with Manufactured Nanomaterials

Non-binding guide for employers and health and safety practitioners

Social Europe

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# Working Safely with Manufactured Nanomaterials

Non-binding guide for employers and health and safety practitioners

## List of Abbreviations

| | |
|---|---|
| **µm** | Micrometre |
| **BAuA** | Bundesanstalt für Arbeitsschutz und Arbeitsmedizin (Germany) Federal Institute for Occupational Safety and Health |
| **CAD** | Chemical Agents Directive 98/24/EC |
| **CLP** | Regulation (EC) n° 1272/2008on Classification, Labelling and Packaging of Substances and Mixtures |
| **CMD** | Carcinogens and Mutagens Directive 2004/37/EC |
| **CMR** | Carcinogen, mutagen and/or reprotoxic substance |
| **CNT** | Carbon nanotubes |
| **CSA** | Chemical Safety Assessment |
| **CSR** | Chemical Safety Report (detailing a Chemical Safety Assessment), as set out by Article 14 of REACH |
| **DNEL** | Derived No Effect Level |
| **EC** | European Commission |
| **EU** | European Union of twenty-eight Member States |
| **GBP** | Granular bio-durable particles without known significant specific toxicity |
| **HARN** | High Aspect Ratio Nanoparticles |
| **HEPA** | High-efficiency particulate air |
| **HSE** | Health and Safety Executive |
| **IARC** | International Agency for Research on Cancer |
| **ISO** | International Organisation for Standardisation |
| **LEV** | Local Exhaust Ventilation |
| **NMM** | Manufactured Nanomaterial; i.e. a nanomaterial which has been deliberately manufactured rather than a nanomaterial which is naturally occurring or arises as an unintended consequence of human activities |
| **MS** | Member States |
| **MWCNT** | Multi wall carbon nanotube |
| **NIOSH** | National Institute for Occupational Safety and Health |
| **nm** | Nanometre |
| **NM** | Nanomaterial, with reference to Commission Recommendation 2011/696/EU on the Definition of Nanomaterial, unless otherwise stated |
| **OEL** | Occupational Exposure Limit value |
| **OSH** | Occupational Safety and Health |
| **PGNP** | Process Generated Nano Particle; a nano particle generated non-intentionally during a process |
| **PM** | Particulate Matter |
| **PPE** | Personal Protective Equipment |
| **PSLT** | Poorly Soluble Low-Toxicity particles |
| **REACH** | Regulation (EC) No. 1907/2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals |
| **REL** | Recommended Exposure Limits |
| **RMM** | Risk Management Measure |
| **SME** | Small and Medium-sized Enterprise (as defined by Commission Recommendation 2003/361/EC) |
| **SWCNT** | Single wall carbon nanotube |
| **TWA** | Time-weighted average |
| **UFP** | Ultrafine particle |
| **WHO** | World Health Organisation |

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# 1 Introduction and background

## The purpose of this Guidance

The purpose of this Guidance is to assist employers, health and safety practitioners and workers in fulfilling their regulatory obligations, namely those under the provisions of Framework Directive 89/391/EEC and the Chemical Agents Directive 98/24/EEC (CAD), whenever exposure to MNMs or use of nanotechnology in a professional capacity is known or likely to take place, with the ultimate aim of ensuring adequate protection of workers' health and safety.

This guidance is provided for general use in occupational settings[1] within the EU in which nanotechnology is used. It does not replace any specific requirements or guidance that may exist at national level, which should be also considered. Also, it should be recognised that nanotechnology is developing fast. Consequently, when drafting this guidance, choices were made with regard to concepts, terminology and methodology which may not be followed elsewhere. Consideration may be given to introducing changes to this Guidance in the future, in the light of relevant developments.

New information, relevant to the protection of workers' health and safety, may become available after the publication of this guidance. It will be important for employers to take any such new information into account when deciding on the most appropriate approaches to risk assessment and risk management at individual workplaces.

This document has been produced for the European Commission as part of a study Service Contract to evaluate the scope and requirements of possible modifications of relevant EU Safety & Health at Work legislation and to elaborate a guidance document to accommodate corresponding risks/concerns (Contract number: VC/2011/0521).

This Guidance document offers an overview of the issues surrounding the safe use of MNMs in the workplace, sets out the broad outlines of preventive action and provides a practical tool for complying with specific aspects of ensuring workers' safety, such as risk assessment and risk management. This may be of particular value to those who may not have an in-depth technical understanding of the issues involved, and may assist in ensuring compliance with the Occupational Safety and Health (OSH) legislation when dealing with MNMs. In particular, this Guidance should assist in addressing any specific risks or concerns about nanomaterials and thus help ensure that they are adequately controlled at the workplace.

Importantly, the procedures and measures suggested by this Guidance are intended to be applied in addition to, and not instead of, the risk assessment procedures and risk management measures normally implemented within the workplace when dealing with chemical agents, in compliance with the provisions of the Chemical Agents Directive 98/24/EC (CAD). **Hence, any suggested measures should be implemented without prejudice to any stricter measures already in place or required by relevant legislation.** For example, when the bulk form of the manufactured nanomaterial has been classified as a carcinogen or mutagen (CM)[2], all appropriate measures according to the occupational

**1** More general information on nanomaterials is available at the following website of the European Commission: http://ec.europa.eu/health/scientific_committees/opinions_layman/nanomaterials/en/index.htm#il1

**2** CM = Carcinogenic, Mutagenic substance, according to the CLP Regulation (EC) No 1272/2008.

legislation for working with substances with CM properties should be applied, namely the Carcinogens and Mutagens Directive 2004/37/EEC (CMD), Directive 92/85/EEC on pregnant workers and workers who have recently given birth or are breastfeeding, and Directive 94/33/EC on the protection of young people at work.

**It must be noted that whenever a MNM is within the scope of CAD, a Risk Assessment should be carried out (Article 4 of CAD).** The scope of CAD is determined by either meeting the criteria for classification as hazardous laid down in Regulation (EC) No. 1272/2008 (CLP) or when a MNM presents a risk to workers' health and safety, according to Article 2(b) (iii) of CAD.

A MNM may have specific characteristics that could result in the material showing special performance properties of value to industry. At the same time, these special properties may also result in a distinctive 'hazard profile', which may be different for each MNM of the same chemistry. As such, the potential risks from the use of a MNM should be assessed on a case-by-case basis. To date, large gaps exist in scientific understanding of the potential health hazards that could be posed by MNMs. Even for those MNMs which have been relatively well examined, the data generated cannot, or can only to a limited extent, be compared to those for substances in bulk form, since suitable characterisation of samples is often lacking or inadequate[3]. However, it is foreseen that the extensive research programmes being conducted worldwide, for example under the EU Research Programmes (FP7 and Horizon 2020) and the OECD's Sponsorship Programme[4], as well as REACH dossier updates and evaluations[5], will provide specific toxicological and ecotoxicological data for some of the most widely used MNMs. Consequently, because of the present degree of uncertainty, this Guidance approaches the issues relating to the safe use of nanomaterials in the workplace in a precautionary manner.

Recourse to the **precautionary principle** presupposes:

- identification of potentially negative effects resulting from a phenomenon, product or procedure;
- a scientific evaluation of the risk which because of the insufficiency of the data, their inconclusive or imprecise nature, makes it impossible to determine with sufficient certainty the risk in question.

European Commission (2000): Communication on the precautionary principle

At present, the validity of the methods used to assess the health effects of nanomaterials is under debate. The OECD is working on amending existing and developing new test guidelines and guidance documents to assess the hazard potential of nanomaterials. However, the application to nanomaterials of the OECD test guidelines developed for general chemicals has resulted in identification of potential negative effects of MNM justifying recourse to the precautionary principle (a brief review of the evidence raised by toxicological studies is provided in Annex I).

**It must be highlighted that inhalation exposure is of the greatest concern with regard to the effects of particulate nanomaterials on occupational health,** and special attention is being given to studying impacts on the respiratory system and the cardio-vascular system. Dermal exposure is also of importance. However, healthy skin has a better barrier function when compared to the respiratory tract although this barrier function could be limited by skin lesions, strong mechanical strain or small nanoparticles (<5 to 10 nm) (EU-OSHA, 2009). **Exposure by ingestion is of lower concern within the workplace; following good personal hygiene and basic safety practice rules (such as washing hands with soap and water before breaks and at the end of the workday, not wearing personal protective clothing outside of work areas and not taking them home for cleaning) should avoid any oral uptake.**

Given the level of uncertainty, the risk assessment proposed in this Guidance places a strong focus on consideration of exposure while still trying to prioritise attention towards those MNMs for which specific health concerns have been raised. Hence, the categorisation of the extent of control needed is based on the physicochemical characteristics of the MNMs and the level of exposure for each task of the work process, directing the user to relevant sources of information and suggesting the level of control corresponding to the potential risk and the degree of associated uncertainty. Given the current lack of specific information related to the nanoform of the chemicals on Safety Data Sheets, the proposed categorisation draws on information about those physicochemical characteristics that should be readily available to the suppliers of the chemicals. It should be noted that, according to Articles 31 and

**3** UBA et al (2013): Nanomaterials and REACH, Background Paper on the Position of German Competent Authorities, Umwelt Bundes Amt. Available at: http://www.bfr.bund.de/cm/349/nanomaterials-and-reach.pdf.

**4** A further twelve MNMs (Fullerenes $C_{60}$, SWCNTs, MWCNTs, Iron nanoparticles, Cerium oxide, Zinc oxide, Dendrimers, Nanoclays and Gold nanoparticles, as well as Silver nanoparticles, Titanium dioxide and Silicon dioxide) are currently being tested and evaluated for 59 defined endpoints relevant to environmental safety and human health. Source: http://www.oecd.org/chemicalsafety/nanosafety

**5** Currently, three substances in nano-form (silicon dioxide, silver and titanium dioxide) are planned to undergo the Substance Evaluation process under REACH. Source: http://echa.europa.eu/regulations/reach/evaluation/substance-evaluation/community-rolling-action-plan

32 of the (EC) Regulation No. 1907/2006 (REACH), it is the duty of the supplier to communicate down the supply chain "any other available and relevant information about the substance that is necessary to enable appropriate risk management measures to be identified and applied…" (Art. 32(1)(d)). Consequently, any downstream user, in order to comply with the CAD and carry out a risk assessment to identify the appropriate RMMs, can ask for further information (free of charge[6]) from the supplier about at least the size and shape of the particles of the substance/mixture and its solubility characteristics. Comprehensive toxicological research has shown without any reasonable doubt that the inhalation of biopersistent/poorly soluble particles can have harmful effects on the respiratory system under certain exposure conditions and that some types of fibre-shaped nanomaterials might have toxicological characteristics similar to asbestos[7] (EU OSHA, 2009).

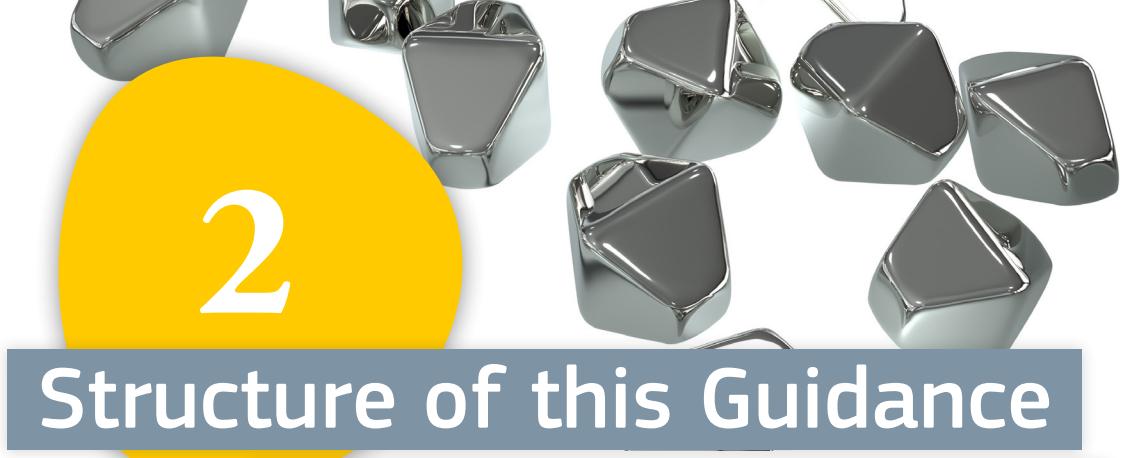
Although **the focus of this Guidance is on MNMs,** some of the risk management measures suggested could contribute to minimising exposure to naturally occurring nanomaterials and incidental nanomaterials (also known as process-generated nanoparticles – PGNPs). Simultaneous exposure to MNMs and to PGNPs may occur in many workplaces and it is advised to take **all potential sources** of nanoparticles (i.e., the total exposure load) into account when undertaking a workplace risk assessment to define the necessary risk management practices.

It should also be noted that several authoritative European and non-European bodies (e.g. ISO and NIOSH) have previously published guidance on the safe use of nanomaterials, including in some instances guidance specific to particular MNMs or specific use scenarios. Users of this Guidance document are advised to also consider these additional other sources of information, as appropriate (see Annex II).

Importantly, the present Guidance should be regarded as a 'living document' which represents the knowledge of nanomaterials and understanding of health and safety issues pertaining to them at the time of writing (June 2014). It may be revised as necessary in the light of new developments. Anyone using this Guide should ensure that they keep up-to-date with this rapidly developing field of knowledge, for example by monitoring the websites listed in Annex II of this Guide. They should also be aware of the need to review their risk assessments for nanomaterials often, in order to take advantage of the latest scientific and medical understanding and, subsequently, to consider whether risk management practices require any amendment.

**6** Article 32(2) of the REACH Regulation.

**7** EU-OSHA (2009): Workplace exposure to nanoparticles, European Risk Observatory Literature Review, the European Agency for Safety and Health at Work (EU-OSHA), available from the EU-OSHA Internet site: http://osha.europa.eu/en/publications/literature_reviews/workplace_exposure_to_nanoparticles



# 2 Structure of this Guidance and reference to Directive 98/24/EC

Section 3 provides an introduction to the terminology used in this Guidance, while Section 4 summarises the suggested risk assessment and risk management procedures. Table 2.1 sets out the correspondence between the contents of this Guidance document and the provisions of the Chemical Agents Directive 98/24/EC (CAD)[8].

**8** Full text available at: http://eur-lex.europa.eu/legal-content/FR/TXT/PDF/?uri=CELEX:31998L0024&from=EN

**Table 2.1: Contents of this Guidance and their correspondence with the CAD**

| Section | Reference in CAD |
|---|---|
| 4.1 Step 1 – Identification of the MNMs | **Article 4(1)** "...determine whether any hazardous chemical agents are present at the workplace" |
| 4.2 Step 2 – Hazard Assessment | **Article 4(1)** Article 4(1) "(...) assess any risk to the safety and health of workers arising from the presence of those chemical agents, taking into consideration..." |
| 4.3 Step 3 – Exposure Assessment | **Article 4(2)** "The risk assessment shall be documented in a suitable form according to national law and practice..."<br><br>**Article 4(3)** "Certain activities within the undertaking or establishment, such as maintenance, in respect of which it is foreseeable that there is a potential for significant exposure, or which may result in deleterious effects to safety and health for other reasons, even after all technical measures have been taken, shall be included in the risk assessment" |
| 4.4 Step 4 – Characterisation of Risk (Control Banding) | **Article 4(2)** "The risk assessment (...)may include a justification by the employer that the nature and extent of the risks related to chemical agents make a further detailed risk assessment unnecessary" |
| 4.5 Step 5 – Detailed Risk Assessment | **Article 6(4)** "Unless the employer clearly demonstrates by other means of evaluation that (...) adequate prevention and protection have been achieved, the employer shall carry out on a regular basis, and when any change occurs in the conditions which may affect workers' exposure to chemical agents, such measurements of chemical agents which may present a risk to worker's health at the workplace as are necessary, in particular in relation to the occupational exposure limit values" |
| 4.6 Step 6 – Risk Management<br><br>4.7 Information, instruction and training<br><br>4.8 Medical Surveillance | **Article 5** General principles for prevention of risks (...)<br><br>**Article 6** Specific protection and prevention measures<br><br>**Article 7** Arrangements to deal with accidents, incidents and emergencies<br><br>**Article 8** Information and training for workers<br><br>**Article 10** Health surveillance<br><br>**Article 11** Consultation and participation of workers |
| 4.9 Step 7 – Review | **Article 4(2)** "The risk assessment shall be kept up-to-date, particularly if there have been significant changes which could render it out-of-date..."<br><br>**Article (5)** "In the case of a new activity involving hazardous chemical agents, work shall only commence after an assessment of the risk of that activity has been made and any preventive measures identified have been implemented" |

# 3 Terminology and Definitions

## What are nanomaterials?

In order for the user to correctly interpret this Guidance, an introduction to the relevant terminology on nanotechnology is provided here.

Many definitions have been discussed by international organisations, national authorities and scientific committees. For an extensive review of the working definitions at national and international level, please consult the JRC Reference Report (JRC, 2010).

**For the purpose of this Guidance, the European Commission's currently recommended definition[9] (provided in Box 1) has been used.**

**9** Available at: http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2011:275:0038:0040:FR:PDF

**Box 1 Definition of a nanomaterial**

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.

In specific cases and where warranted by concerns for the environment, health, safety or competitiveness the number size distribution threshold of 50 % may be replaced by a threshold between 1 and 50 %.

By derogation [from the above], fullerenes, graphene flakes and single wall carbon nanotubes with one or more external dimensions below 1 nm should be considered as nanomaterials.

Within this definition of nanomaterials, the terms "particle", "agglomerate" and "aggregate" are defined as follows:

- "Particle" means a minute piece of matter with defined physical boundaries;
- "Agglomerate" means a collection of weakly bound particles or aggregates where the resulting external surface area is similar to the sum of the surface areas of the individual components;
- "Aggregate" means a particle comprising strongly bound or fused particles.

Where technically feasible and requested in specific legislation, compliance with the definition [of a nanomaterial] may be determined on the basis of the specific surface area by volume. A material should be considered as falling under the definition where the specific surface area by volume of the material is greater than 60 m2/cm3. However, a material which, based on its number size distribution, is a nanomaterial should be considered as complying with the definition even if the material has a specific surface area lower than 60 $m^2/cm^3$.

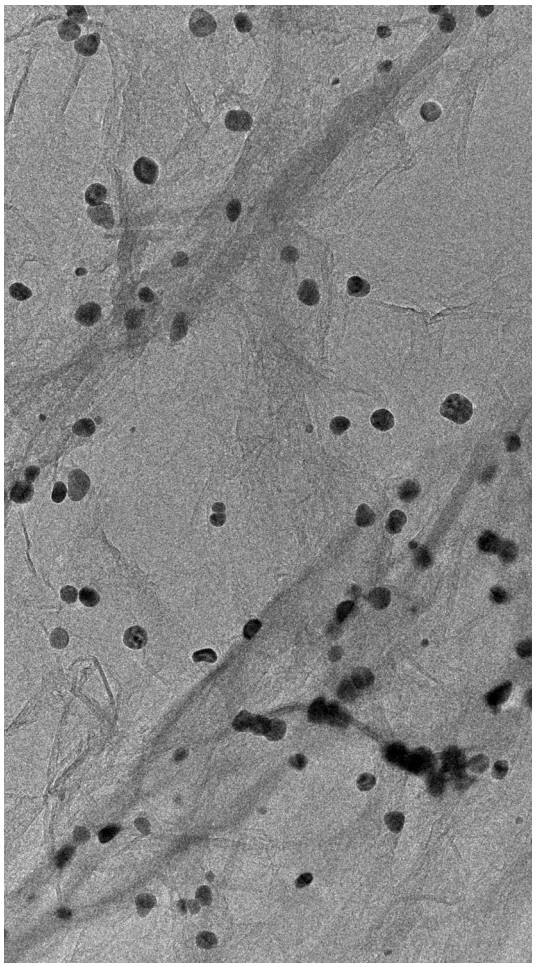
European Commission, Recommendation 2011/696/EU.

A review (1st step before a possible revision) of this definition is due by December 2014.

Nanotechnology has been identified as a key enabling technology (KET) providing the basis for further innovation and new products. Products using nanotechnology are increasingly finding application within European industries. As a result, the potential risks arising from the use of nanomaterials may be present in many different sectors and work activities. Annex III provides a non-exhaustive list of the main applications of some of the most used MNMs..

The intrinsic properties (physicochemical and toxicological) of chemical agents (and thus of nanomaterials) constitute the hazards which have the potential to cause harm (hence needing to be assessed – hazard assessment), while the way they are used or are present in the workplace (exposure) determines the likelihood that the potential for harm will be attained (hence the need for an exposure assessment). Further clarification on the applicability of the CAD to nanomaterials is provided in Annex IV.

Although this Guidance attempts to provide concise and easily understandable information for a non-specialised audience, the use of some technical words and concepts is unavoidable when dealing with nanotechnology. In order to clarify such terms, their definitions have been provided below. Some of these are consistent with the terminology as elaborated and used by other organisations[10] and in any case consistent with the current EC recommended definition of nanomaterials.



- **Nanoscale** is the size range from approximately 1 nm to 100 nm (NOTE 1: Properties that are not extrapolations from a larger size will typically, but not exclusively, be exhibited in this size range. NOTE 2: The lower limit in this definition (approximately 1 nm) has no physical significance but is introduced to avoid single and small groups of atoms from being designated as nano-objects or elements of nanostructures, which might be implied by the absence of a lower limit) (BSI, 2007).

- **Nano-object** is a discrete piece of material with one or more external dimensions in the nanoscale (NOTE: This is a generic term for all nanoscale objects) (BSI, 2007).

- **Nanoparticle** is a nano-object with all three external dimensions in the nanoscale (NOTE: If the length of the longest and the shortest axes of the nano-object differ significantly (typically by more than three times) the terms nanorod or nanoplate are intended to be used instead of the term nanoparticle) (BSI, 2007).

- **Nanopowder** is a mass of dry nanoparticles (BSI, 2007).

- **Ultrafine particles (UFPs)** make up the smallest fraction of ambient particulate matter (PM) and are defined as airborne particles with a diameter in the nanoscale (HEI, 2013). In this Guidance, the term “ultrafine particles” is used when referring to naturally-occurring nanomaterials.

- **Process-generated nanoparticles (PGNPs)** or incidental nanomaterials, are particles generated incidentally during work activities, e.g. by electrical machines, heating, welding and combustion processes.

- **Nanofibre** is a nano-object with two similar external dimensions in the nanoscale and the third dimension significantly larger. A nanofibre can be flexible or rigid. The two similar external dimensions are considered to differ in size by less than three times and the significantly larger external dimension is considered to differ from the other two by more than three times. The largest external dimension is not necessarily in the nanoscale (ISO/TS 27687:2008). If the nanofibre has a length greater than 5 µm, a width less than 3 µm and a length to width ratio (aspect ratio) greater than 3:1, it meets the WHO criteria and, within this Guidance, is called a WHO nanofibre.

- **High Aspect Ratio Nanoparticles (known as HARNs)** are particles with one or two dimensions in the nanoscale that are much smaller than the others (HSE, 2013). Besides nanofibres, nanoplatelets (that present only one dimension in the nanoscale) are considered HARNs.

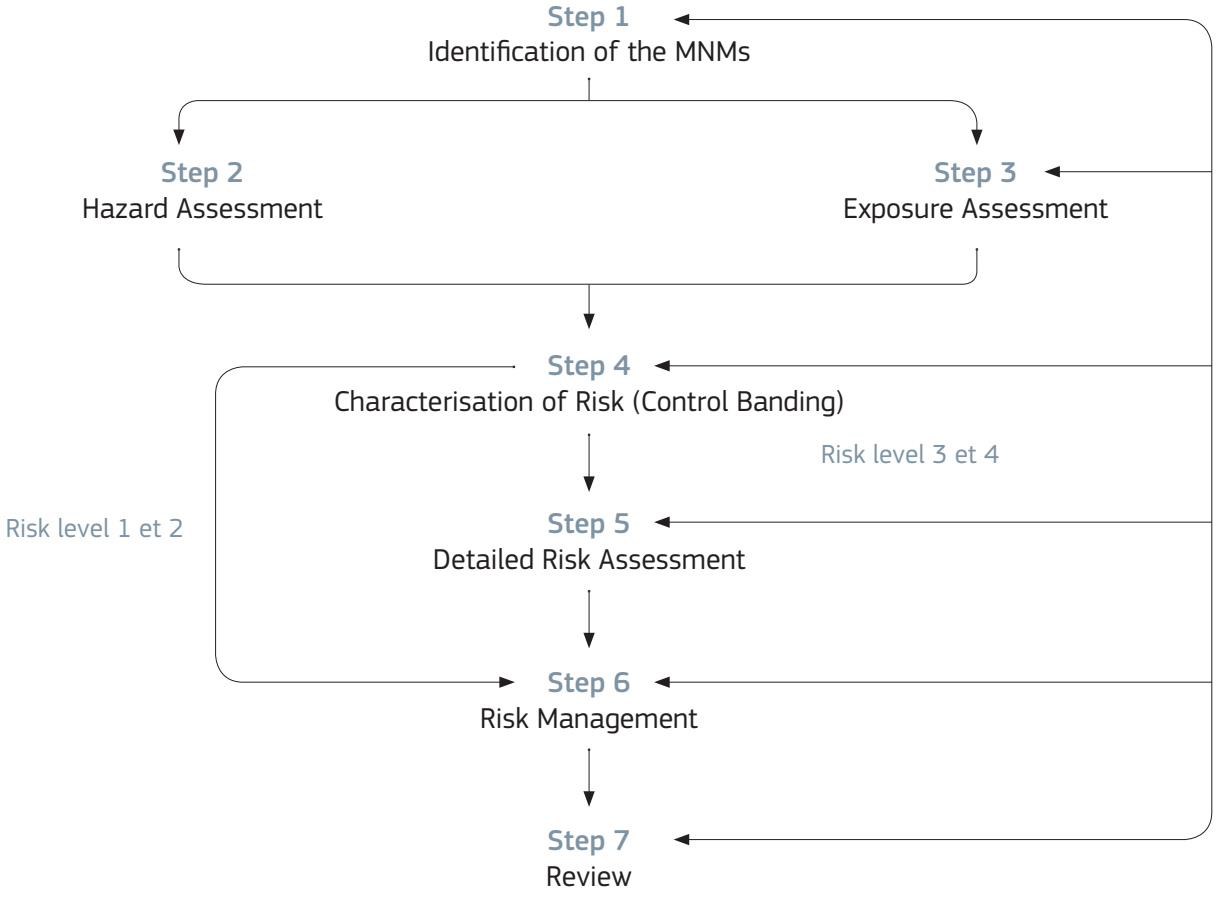
**10** e.g. the British Standard Institution (BSI) in the Publicly Available Specification (PAS) on the terminology for nanomaterials and the International Standard Organisation, in particular the Technical Committee 229, in the Technical Specifications for the terminology to be used in the nanotechnology field, most importantly:

- ISO/TS 27687:2008 “Nanotechnologies – Terminology and definitions for nano-objects – Nanoparticle, nanofibre and nanoplate”;
- ISO/TS 80004-1:2010 “Nanotechnologies - Vocabulary - Part 1: Core terms”; and
- ISO/TS 80004-3:2010 “Nanotechnologies - Vocabulary - Part 3: Carbon nano-objects”.


# 4 Risk Assessment and Management Process

The employers' obligations for ensuring the protection of the health and safety of workers from the risks related to hazardous chemical agents at work are set out in Section II of the CAD. As for any chemical, it is the duty of employers to carry out a Risk Assessment whenever MNMs are handled during work activities. Figure 4.1 shows the various steps involved in risk prevention when working with MNMs. Each step is detailed in the sections that follow. The risk assessment and the efficacy of the implemented risk management measures must be reviewed periodically and before any changes are made to either the chemical agents being used or working conditions (in compliance with CAD Article 4(5)).

**Figure 4.1: Diagram for Risk Assessment**



## 4.1 STEP 1 – IDENTIFICATION OF THE MNMS

**Article 4(1)** of the CAD first requires employers to determine whether any hazardous chemical agents are present at the workplace. In addition, employers that are uncertain about the **presence of MNMs in the workplace** should check the inventories of substances used or supplied to verify whether any are identified as MNMs or may contain MNMs.

Primary sources of information are the Safety data sheets (SDS) accompanying the substances/mixtures used in the workplace. Although, according to article 31 of the REACH Regulation, their provision is mandatory only for those substances and mixtures that are classified under the CLP Regulation or meet the criteria set out in Annex XIII of the REACH Regulation as being classified as persistent, bioaccumulative and toxic or very persistent and very bioaccumulative, it is commonly the practice of the chemical industry to provide a SDS for non-classified substances/mixtures as well.

If a SDS is not needed (no classification according to CLP) and not supplied information may be found online from other suppliers; the quality of this information may need checking. More information can be found on the ECHA website[11]. In particular, information about the form of the substance or the presence of MNMs in a mixture might be found in the following sections of a SDS:

1. Identification of the substance/mixture and of the company/undertaking;
3. Composition/information on ingredients;
9. Physical and chemical properties.

**Where there is uncertainty, employers should contact the suppliers/manufacturers of the substances/mixtures to specifically request the necessary information.**

## 4.2 STEP 2 – HAZARD ASSESSMENT

### 4.2.1 GENERAL RISK CONSIDERATIONS

If MNMs are present in the workplace, the employer shall then assess **any risks to the safety and health of workers.** Table 4.1 (reproduced and adapted from EC, 2004[12]) summarises the risks to be assessed under the CAD and provides a non-exhaustive list of risk factors related to the presence of hazardous chemical agents. Some risk factors to which particular attention should be paid during the risk assessment of MNMs have been highlighted in bold.

**11** http://echa.europa.eu/fr/information-on-chemicals/registered-substances

**12** EC (2004): Practical Guidelines of a non-Binding Nature on the Protection of the Health and Safety of Workers from the Risks Related to Chemical Agents at Work.

**Table 4.1: Risks arising from the presence of MNMs**

| Risk | Some risk factors |
|---|---|
| Risks due to inhalation of the agent | • Toxicity of the MNM<br>• **Physicochemical characteristics of the MNM**<br>• Environmental concentration<br>• Exposure time<br>• Particularly sensitive workers<br>• **Inappropriate selection and/or use of RPE** |
| Risks due to absorption through the skin | • Location and extent of the contact with the skin<br>• Toxicity of the MNM agent via the skin<br>• Duration and frequency of contact<br>• Particularly sensitive workers<br>• **Inappropriate selection and/or use of PPE** |
| Risks due to contact with the skin or eyes | • **Inappropriate selection and/or use of PPE**<br>• Inappropriate work procedure<br>• Incorrect transfer procedure |
| Risks due to ingestion | • Toxicity of the MNM<br>• **Potential toxicity of the MNM**<br>• Incorrect personal hygiene habits<br>• Possibility of eating, drinking or smoking in the workplace<br>• Particularly sensitive workers |
| Risks of fire and/or explosion | • **Physical state (ultrafine dust)**<br>• Pressure/temperature<br>• Flammability/calorific value<br>• **Airborne concentration**<br>• Sources of ignition |
| Risks due to hazardous chemical reactions | • Chemical reactivity and instability of hazardous chemical agents<br>• Inadequate cooling systems<br>• Unreliable system for controlling key variables in the reaction (pressure, temperature and flow control) |
| Risks arising from installations which may have consequences on the health and safety of workers | • Corrosion of materials and installations<br>• Deficient or non-existent facilities for controlling leaks and spills (retaining trays, protection against mechanical impacts)<br>• Deficient or non-existent preventive maintenance |

To determine the capacity of chemical agents (and thus of MNMs) present in the workplace to cause risk, the hazardous properties of these agents and the exposure, i.e. the way in which they are used or are present, must be known. Normally, information on the hazardous properties of chemical agents present in the workplace can be obtained from:

- Labels (pictograms);
- Safety data sheets;
- European Commission recommendations;
- Occupational exposure limit values; and
- Other sources (peer reviewed data, scientific literature, relevant databases, etc.).

Currently, specific information on the physicochemical characteristics of MNMs is not reported in SDS. Moreover, toxicological and ecotoxicological data specific to MNMs may be lacking. Different international organisations (such as the OECD) are working on adapting existing or developing new standardised testing methodologies for nanomaterials and are in the process of generating further relevant information for some widely used MNMs. In the meantime, simplified risk assessment procedures have been developed to overcome these shortcomings.

Several lists of physicochemical parameters for the characterisation of nanomaterials have been proposed and the way they influence the toxicological profile of MNMs is being discussed. However, some hazardous properties are known from the macro material form, for example highly reactive materials can be expected to cause toxic effects if they are inhaled or absorbed into the body, as these types of properties are known to be significant factors in the toxicity of macro form materials. Similarly, **if the macro form of a substance is classified as a carcinogen, mutagen or reproductive toxin (CMR), as a sensitiser, or for another significant toxicity, then it should be assumed that the nanoform will also show these properties unless proven otherwise.** Although, presently, it is still uncertain which parameters represent the best predictive value for toxicity, there is growing evidence that for nanomaterials a high aspect ratio and poor solubility might lead to negative effects on human health.

As detailed in Annex I, most concerns regarding MNMs have centred on the possible consequences of inhalation exposure, as nanoparticles may be carried deep into the lungs and there are concerns that they may have the ability to elicit acute or chronic inflammatory responses.

Particular care is suggested when considering the risks that may be posed by nanoparticles possessing certain physical aspect characteristics. In particular, attention has focused on the so called "High Aspect Ratio Nanoparticles" (HARNs) because of suggested similarities in their physical characteristics to materials known to be hazardous, such as asbestos or some man-made mineral fibres. Poland and Donaldson[13] suggested that HARNs may be retained in the pleural cavity for long periods of time[14] if they show the additional characteristics:

- Thinner than 3 µm
- Longer than 10-20 µm
- Biopersistent, and
- Which do not dissolve/break into shorter fibres[15]

As for nanofibres, concerns have been raised over nanoplatelets (considered HARNs) and their aerodynamic behaviour which might result in them penetrating deep within the lung (HSE, 2013).

Water solubility is another factor that may influence toxicity. In order to overcome the lack of specific data on biopersistence of MNMs, water solubility is used in this Guidance as a proxy for possible biopersistence. See more detailed explanations on this parameter under section 4.2.2 of this document.

In order to comply with CAD **Article 4(1), the employer should obtain additional information needed for the risk assessment from the supplier or from other readily available sources and, as a minimum, this should include information on the size and shape of the particles of the substance/ mixture and its solubility and/or biopersistence characteristics.** It must be noted that "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" (HSE, 2013). For example, carbon nanotubes do not have identical inherent properties and not all of them have caused equal high concern for possible effects on human health.

Forms which do not differ significantly in terms of their physicochemical characteristics can be regarded as comparable. To date, however, it is not possible to determine what degree of variation is acceptable for each individual parameter (UBA et al, 2013).

It should be noted that Article 4(1) of CAD states that the employer shall obtain from the supplier additional information on the hazardous properties of a substance, when it is needed for the risk assessment, and Article 8.3 lays down that Member States may take measures to ensure that this information can be obtained. On the other hand, according to Articles 31 and 32 of REACH, **suppliers of substances and mixtures have a duty to pass on any available information needed for a downstream user to carry out a risk assessment.** In the absence of specific toxicological information on MNMs, employers therefore have the right to ask, free of charge, for relevant physicochemical information sufficient to allow at least a partial characterisation of the MNMs and of their potential hazard profile (see table 4.2).

If the information available is not sufficient for the characterisation of the MNM in order to carry out the simplified risk assessment detailed in this Guidance, **the employer should adopt a reasonable worst case scenario approach, taking account of the available evidence and in the light of the precautionary principle.**

**13** http://www.safenano.org http://www.particleandfibretoxicology.com/content/7/1/5/abstract

**14** Mechanism known as "frustrated phagocytosis", the incomplete engulfment of a particle by a cell, leading to failure to remove the particle form the body and a risk of cell damage and release of harmful endogenous substances into the body.

**15** The hazards characteristics of HARNs with a length below 5 µm are (probably) the same as for granular particles. However, as the length distributions of samples of HARNs usually exhibit wide variations, a sample with a median length of 1.5 µm could still contain a considerable number of individual HARNs with a length > 5 µm.

Table 4.2 presents the data that should be gathered, as a minimum, to allow the simplified Risk Assessment procedure proposed in this Guidance to be carried out.

**Table 4.2: Characterisation data**

| Minimum Information | Material example for Minimum Information |
|---|---|
| Chemical name and product name | e.g. Nanosilver |
| Manufacturer/supplier company name | If you are the manufacturer, please insert the name of your company |
| CAS Number and EC Number | e.g. CAS Number 7440-22-4, EC Number 231-131-3 |
| Chemical Formula/Chemical Structure | e.g. Ag |
| Intended Purpose of the MNM | e.g. the MNM increase the protection against weathering |
| Physical Hazard Classification of the bulk form* | Hazard Class and Category Code(s) (e.g. Expl. 1.1) and/or text defining the appropriate Hazard Statements |
| Health Hazard Classification of the bulk form* | e.g. Acute Tox. 1 or H300 |
| Environmental Classification of the bulk form* | e.g. Aquatic Acute 1 or H059 |
| Appearance | Physical state, granulometry and specific surface area |
| Surface Composition | If the MNM is modified, functionalised or coated with a chemical, please seek expert advice |
| Geometry/Shape, rigidity | e.g. particulate or fibrous, rigid or flexible |
| Number Particle Size Distribution | |
| Water solubility | e.g. 45 mg/l |
| Dustiness | |
| Flammability | |

**Notes:**

***** Please consider that if the bulk form of the nanomaterials you handle have been classified under the CLP Regulation (EC) No 1272/2008, you should apply, as a minimum, the Risk Management Measures required by the relevant legislation and indicated on the Safety Data Sheet.

### 4.2.2 CATEGORISING LEVEL OF CONCERN – SHAPE AND SOLUBILITY

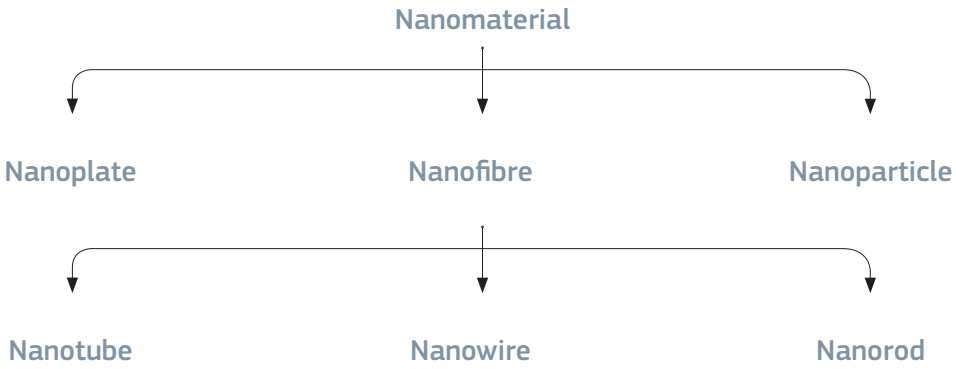
A categorisation rating for the level of concern relating to the possible effects of MNMs on workers' health based on the geometry/shape and persistence/ water solubility characteristics is proposed below in Table 4.3. For proper categorisation, a thorough understanding of these concepts is important.

**Table 4.3: Concern Categorisation**

| Concern Category | Characteristics of the MNM | NMM 1 | NMM ... |
|---|---|---|---|
| High Concern | Poorly soluble or insoluble (water solubility <100 mg/l) WHO nanofibres | ☐ | ☐ |
| Medium-High Concern | Poorly soluble or insoluble (water solubility <100 mg/l) nanoparticles with specific toxicity and poorly soluble or insoluble HARNs other than poorly soluble or insoluble WHO nanofibres | ☐ | ☐ |
| Medium-Low Concern | Poorly soluble or insoluble nanomaterials with no specific toxicity | ☐ | ☐ |
| Low Concern | Soluble nanomaterials | ☐ | ☐ |

- **Shape** - ISO defines the shape of particles on the basis of the number of dimensions in the nanoscale. A nanoplate is a particle with only one dimension in the nanoscale, a nanofibre is a particle with two dimensions in the nanoscale and the third dimension significant larger, while a nanoparticle is a particle with all three dimensions in the nanoscale. A hollow nanofibre is called a nanotube, a flexible nanofibre is called a nanowire and a rigid nanofibre is called a nanorod. Figure 4.2 provides a schematic representation of the types of nanomaterials based on shape.

**Figure 4.2: Schematic representation of types of nanomaterials based on shape**




- **Persistence** – Persistence is primarily used in a risk assessment context to define chemicals or materials which are retained in the body or in the environment beyond a defined amount of time. A persistent material is a material poorly soluble/insoluble and resistant to breakdown into smaller structures and molecules. For example, with respect to fibrous materials, the term biopersistence can be defined as the ability to resist removal from the lungs by natural mechanisms like dissolution. In this case, the measure used is the half-life, i.e. the time needed for 50% of the fibres to be removed from the lungs. Macrophages play an important role in the clearance of short fibres by phagocytosis. However, for long, rigid and poorly soluble fibres, the process of phagocytosis is hampered because the fibre cannot be "swallowed" completely by the macrophage.

- **Water Solubility** – Water solubility (usually expressed in mg/l) is the highest amount of a substance that can be dissolved in a specific volume of water. The solubility of the bulk form may differ significantly from the solubility of the nano-size form. The threshold of 100 mg/l is usually indicated to distinguish between soluble and poorly soluble/insoluble (nano)materials. In order to overcome the lack of specific data about the biopersistence of MNMs, water solubility is used in this Guidance as a proxy for biopersistence. In terms of solubility only, poorly soluble or insoluble nanomaterials are considered of concern; soluble nanomaterials (with a water solubility above 100 mg/l) are considered of no concern. However, in some cases, a material may show a poor solubility in water but a good solubility in biological media as, for example, cobalt which is insoluble in water but soluble in serum.

With the possible exception of amorphous silica, all the nanomaterials currently produced in high volume[16] are poorly soluble/insoluble.

**16** For example: amorphous silica, silver, titanium dioxide, fullerenes $C_{60}$, SWCNTs, MWCNTs, iron nanoparticles, aluminium oxide, cerium oxide, zinc oxide, nanoclays and gold nanoparticles).

## CONCERN CATEGORIES[17]

**17** The categories of concern are defined at present drawing essentially on the likely impact that the nanoform of a substance may have; in specific cases the same effects may be caused by the substance in non-nanoform.

**High concern** - poorly soluble or insoluble nanofibres are of the highest concern: toxicological studies demonstrated that long fibres retained in the pleural cavity can cause persistent inflammation and might lead to long-term health effects such as fibrosis and lung cancer. Although evidence of toxic effects has been identified for rigid fibres longer than 10-20 µm, all the fibres with a length of more than 5 µm (fibres meeting the WHO criteria), regardless of their rigidity, should be considered of high concern, since "fluffy" nanofibres might be tangled together and behave as rigid fibres within the body. Some types of CNTs match these characteristics and should be regarded as of high concern.

**Medium-high concern** - Poorly soluble or insoluble (with water solubility of less than 100 mg/l) nanoparticles with specific toxicity and poorly soluble/insoluble High Aspect Ratio Nanoparticles other than poorly soluble or insoluble WHO nanofibres should be regarded as of medium-high concern. This category encompasses those nanomaterials with toxic properties and those nanomaterials for which the macroform of the substance possesses toxic properties and there are no data showing that the nanoform does not present the same properties. Moreover, those poorly soluble or insoluble HARNs that are not included in the high concern category (nanoplatelets, nanofibres with a length of less than 5 µm) should be considered of medium-high concern due to their ability to penetrate deep into the lungs which may result in inflammatory reactions. Examples of medium-high concern nanomaterials include nanosilver, gold nanoparticles and zinc oxide nanoparticles.

**Medium-low concern** - Poorly soluble or insoluble nanomaterials with no specific toxicity and that do not present a high aspect ratio are of medium-low concern: these MNMs do not present specific toxic properties beyond those owned by the substance. Examples are carbon black and titanium dioxide.

**Low concern** – All nanomaterials with a water solubility above 100 mg/l should be regarded as of low concern with regard to nano-specific toxicological effects. Due to their solubility, the nanoparticle should not be retained into the body for a period long enough to cause nano-specific adverse health effects. Examples of MNMs in this category are: sodium chloride nanoparticles, lipid-nanoparticles, flour nanoparticles, sucrose-nanoparticles and amorphous silica.

### 4.2.3 CATEGORISING LEVEL OF CONCERN – DUSTINESS AND FLAMMABILITY

**Dustiness** – Dustiness may be defined as the propensity of a solid to form airborne dust when mechanically processed. Table 4.4 reproduces for the convenience of the Guidance user, the dustiness bands proposed in ECHA (2012)[18].

**Flammability** – Flammability is a concept related to the easiness of a substance to ignite or sustain a combustion reaction. By and large, nanoscale metal powders are easily ignitable, while carbon nanomaterials are not (safe work Australia, 2013)[19]. Fully oxidised materials, such as silicon dioxide, cerium dioxide and zinc oxide do not ignite or sustain a combustion reaction.

**Table 4.4: Dustiness bands**

| Band | Dustiness |
|---|---|
| High | Fine, light powders. When used, dust clouds can be seen to form and remain airborne for several minutes. For example: cement, titanium dioxide, photocopier toner |
| Medium | Crystalline, granular solids. When used, dust is seen, but it settles quickly. Dust is seen on the surface after use. For example: soap powder, sugar granules |
| Low | Pellet-like, non-friable solids. Little evidence of any dust observed during use. For example: PVC pellets, waxes |

**18** ECHA (2012): Guidance on information requirements and chemical safety assessment, Chapter R.14: Occupational exposure estimation, version 2.1 – November 2012.

**19** Safe work australia (2013): Safety Hazards of Engineered Nanomaterials, Information sheet, available at: https://www.safeworkaustralia.gov.au/system/files/documents/1702/safety-hazards-engineered-nanomaterials.pdf

**20** This list is proposed in goodnanoguide.org, available at Internet site: http://www.goodnanoguide.org/Assess+Potential+Exposures

**21** These questions were proposed in CSIRO (2012): Safe handling and use of Carbon NanoTubes, prepared for Safe Work Australia, and adapted accordingly.

## 4.3 STEP 3 – EXPOSURE ASSESSMENT

A key part of any risk assessment is a thorough understanding of the exposure potential for workers.

For each MNM, routine workplace activities and other foreseeable events (e.g. accidental spills or other equipment failure scenarios) which may potentially result in the release of the MNM and subsequent exposure of workers should be defined. A list of generic activities[20] which may apply to the life-cycle of each MNM is presented below:

- Material Receipt, Unpacking and Delivery;
- Laboratory Operations;
- Manufacturing and Finishing;
- Cleaning and Maintenance;
- Storage, Packaging and Shipping;
- Waste Management;
- Reasonable Foreseeable Emergencies.

For each work activity involving the manufactured nanomaterial, as appropriate, you should ask the following questions[21]:

- What are the tasks where the workers are exposed to MNMs?
- Is the material dusty or the process likely to generate dusts or aerosols of MNMs?
- Does the process include cutting, shearing, grinding, abrasion, or other mechanical release of MNMs or materials containing MNMs?
- What is the physical state of the MNMs in each stage of the work process? (i.e. **Dry powder / suspension or liquid / embedded or bound in other materials)**
- What are the potential routes of human exposure? (e.g., inhalation, dermal absorption)
- What is the chance of exposure occurring? Consider not just exposures during normal routine working but also possible accidental releases and maintenance.
- How often is exposure likely to occur, for example continuously over a working shift, intermittently, rarely?

For the convenience of users of this Guidance, Table 4.5 provides a list of possible work activities involving the handling of MNMs. The table should be modified accordingly if necessary and used for the recording of information relevant for the Exposure Assessment.

Emissions of dust/mist/haze may have already been prevented by risk management measures (RMMs) introduced to reduce risks of other (non-nano) chemical agents. In this case, the efficacy of these RMMs in minimising workers' exposure to MNMs should be verified. The information sheets provided with the installed equipment/personal protective equipment might report on their efficacy for the different forms of the chemical agents. If this information is not available, the employer should ask the supplier of the equipment or seek expert advice.

**Table 4.5: Activities involving potential exposure to MNMs**

| Name of the MNM(s): ..... | | | | | |
|---|---|---|---|---|---|
| **Activity** | **Amount (kg, l)** | **Dust emission (yes/no)** | **Duration (minutes)** | **Frequency (times per d/w/m)** | **No and ID of workers** |
| Manufacturing of the MNM | | | | | |
| Reception and storage of the MNM | | | | | |
| Transport in the facility (fork truck, manual , etc.) | | | | | |
| Operating machines | | | | | |
| Handling (opening vessels, valves, seals, emptying sacks, brushing, spraying…) | | | | | |
| Machining (drilling, abrasion, polishing…) | | | | | |
| Filtering/separation | | | | | |
| Sampling (quality control) | | | | | |
| Filling/packaging of end product | | | | | |
| Cleaning and maintenance of equipment | | | | | |
| Cleaning working area (e.g. floor, walls, etc.) | | | | | |
| Transport outside (container by road/ sea/air…) | | | | | |
| On-site treatment of waste | | | | | |
| Collection of waste | | | | | |
| Removal of waste | | | | | |
| Emergencies | | | | | |
| Other activities… | | | | | |

Based on the information collected in Tables 4.4 and 4.5, Table 4.6 shows the exposure categorisation according to the characteristics of work activities and the dustiness of the substance/mixture. The exposure assessment should be carried out for each identified MNM for each work activity.

It is worth remembering that, in order to comply with Article 4(2) of the CAD, **all the information gathered for the Risk Assessment should be "documented in a suitable form according to national law and practice…".**

**Tablea 4.6: Work activity exposure assessment**

**Name of the MNM(s): .....**

| Level of exposure | Description | Activity1 | Activity ... |
|---|---|---|---|
| High | **Free/unbound MNMs, dustiness high band, likely emission of MNMs**<br>Tasks that are likely to produce airborne MNMs:<br>• Manufacture of MNMs — e.g. synthesis, "top-down" process<br>• MNM handling in dry state or powder form, e.g. sampling, weighing and measuring, scraping, packing and opening of bags<br>• Spraying of a solution containing MNMs<br>• Cleaning and maintenance of equipment | ☐ | ☐ |
| Medium High | **Possible Emission of MNMs (friable or brittle matrix), dustiness medium band:**<br>• Dry blending of MNMs into a matrix (e.g. polymer)<br>• Processing of solid substances in the nanoform or solid mixtures containing MNMs through, e.g. weave, knit, twist, cut, grind, scrape, etc.<br>• Cutting/grinding a matrix containing MNMs if they can be released from the matrix | ☐ | ☐ |
| Medium Low | **Emission of MNMs anticipated as very low, dustiness low band:**<br>• Extruding and manipulating matrixes containing MNMs (e.g. paints or polymers)<br>• Processing, shaping, moulding of matrixes containing MNMs<br>• Cutting/grinding a matrix containing MNMs if release is unlikely<br>• Solutions containing MNMs are mixed or agitated<br>• MNMs in articles or in fully cured coating on surfaces of articles | ☐ | ☐ |
| Low | **Unlikely emission of MNMs:**<br>• Painting, coating (excluding spraying) or packaging of extruded product<br>• MNMs are embedded in a matrix and no machining | ☐ | ☐ |

## 4.4 STEP 4 – CATEGORISATION OF RISK (CONTROL BANDING)

The simplified risk assessment procedures presented in this Guidance have been developed to assist employers in determining the need for implementing control measures. This section is a general description of the control banding concept and how it could be applied to the risk assessment in the particular case of exposure to nanomaterials.

Some Member States have developed national guidance documents to address this issue (see references in Annex II) and, as mentioned in Section 1, employers should follow any existing national requirements.

The procedure presented in this Guidance is used to determine the risk management measures appropriate for the work activity being assessed. Table 4.7 shows the four potential levels of risk identified by combining the information gathered from the health concern categorisation and from the level of exposure determined for each MNM and work activity. According to the level of risk determined, some technical solutions are provided in the following sections.

**Table 4.7: Control Banding: Risk Level = Concern Category x Level of Exposure**

| | Level of Exposure | | | |
|---|---|---|---|---|
| **Concern Category** | **Low** | **Medium-low** | **Medium-high** | **High** |
| **Low** | 1 | 1 | 2 | 2 |
| **Medium-low** | 1 | 2 | 2 | 3 |
| **Medium-high** | 2 | 2 | 3 | 4 |
| **High** | 3 | 3 | 4 | 4 |

For Risk Level 1 and 2, where the level of exposure is low, medium low and/or the level of concern over the potential hazard of the MNMs is low, medium low, it is considered that adequate prevention and protection can be achieved by implementing standard risk management measures and without the need for additional periodic exposure measurements, as provided by article 6(4) of the CAD. It is left to the judgement of employers to determine whether following this approach will be sufficiently protective of workers' health.

For Risk Level 1 and 2: Section 4.6 provides an overview of the hierarchy of controls and of the risk management measures advisable for the different risk level.

For Risk Level 3 and 4, before implementing any RMMs (presented in Section 4.6), a detailed Risk Assessment should be carried out (as detailed in Section 4.5).

The higher the risk level obtained, the more stringent risk management measures should be taken. In case of uncertainty on the outcome of the control banding approach, a detailed risk assessment, normally including airborne concentration measurements, is needed (see section 4.5). For the higher risks levels 3 and 4 it is advisable to carry out a detailed assessment as a general rule.

According to the Risk Level identified, Table 4.8 can be used to record the appropriate Control Level by MNM and work activity.

**Table 4.8: Record of the appropriate level of control**

| No. | NMM | Activity | Control level | 1 | 2 | 3 | 4 |
|---|---|---|---|---|---|---|---|
| 1 | ... | ... | | ☐ | ☐ | ☐ | ☐ |
| 2 | ... | ... | | ☐ | ☐ | ☐ | ☐ |
| 3 | etc. | etc. | | ☐ | ☐ | ☐ | ☐ |

## 4.5 STEP 5 – DETAILED RISK ASSESSMENT

It is an important principle of occupational health and safety practice to assess potential exposure quantitatively and to verify the adequacy of engineering controls. Particularly in the case of hazardous substances (irrespective of whether they are in nano- or macro-form), regular monitoring of the correct functioning of engineering controls is necessary.

This may be complemented by periodic exposure measurements where suitable sampling and analytical methodologies exist, taking into account any NMN-specific OELs.

In the case of MNMs with no health hazard classifications and for which no European or Member State occupational exposure limits (OELs) have been established, it may be that the manufacturer has established a nano-specific derived no-effect level (DNEL) value in accordance with the REACH regulation (though this would be likely only if the substance had a market volume of >10 tonnes/annum and it is classified according to CLP). In this case, the REACH exposure scenario, attached to the Safety Data Sheet, provides information on Risk Management Measures and Operational Conditions.

For certain nanomaterials, industry and research have suggested either specific OELs or DNELs (these are summarized in Table 4.9 below). Some companies and research institutes have also proposed an OEL for multiwall carbon nanotubes (MWCNTs) (Bayer, Nanocyl and NIOSH); while DNELs were calculated in an experimental study by Stone et al. (2009) applying the DNEL methodology with the prescribed assessment factors to MWCNTs, fullerenes, Ag and $TiO_2$. A threshold value for Carbon Nanotubes has also been set in Switzerland in 2011 by the Swiss National Accident Insurance Fund at 0.01 fibres/ml (SECO, 2012).

Even where no MNM-specific OELs have been defined, consideration may still be given to establishing an exposure monitoring programme (either for ambient air levels in the workplace or for concentration levels in worker's breathing zones using personal sampling devices), where this is judged to be prudent as a precautionary measure. This may be particularly appropriate in the case of MNM falling within the two categories of highest concern. Where there are no obvious criteria against which to judge the acceptability of exposure, it should be noted that some organisations have suggested that – in the absence of OEL or DNEL values – a pragmatic approach would be to compare the extent of nanomaterial exposure against nominal, non-health based, benchmark values. Examples of such benchmark-based approaches include that of the IFA[22] and, in the Netherlands, the use of nano reference values (NRV[23]).

**In any event, as a minimum, it will be necessary to ensure compliance with any existing generic threshold limit values, such as general dust limit-values for alveolar and respirable dust fractions, irrespective of the sources contributing to these fractions (be they MNM or process generated or incidental particles).** The output of such monitoring would assess the appropriateness of the control measures introduced to ensure worker safety with respect to nanoparticle exposure since the nano-fraction of airborne particles will be included in the respirable particle fraction.

**Table 4.9: Suggested RELs and DNELs at March 2013**

| Substance | | REL µg/m³ | DNEL µg/m³ | Reference |
|---|---|---|---|---|
| MWCNT | Long term exposure | | 50 | Pauluhn, 2009 [24] |
| CNT and CNF | 8-hr TWA | 1 | | NIOSH 2013[25] |
| Fullerenes | Chronic inhalation | | 270 | Stone et al 2009[26] |
| Ag (18-19nm) | DNEL | | 98 | Stone et al 2009 |
| $TiO_2$ (10-100 nm) (REL) | 10hr/day, 40hr/week | 300 | | NIOSH 2011[27] |

Undertaking a robust monitoring program on nanoparticles or nanofibres is, however, challenging: at the time of writing, no official occupational exposure limits (OELs) specific to nanomaterials have been set at EU level, sampling and measurement methods are being researched and simple methods for practical monitoring of exposure in commercial enterprises do not exist yet (see Annex V). **Under such circumstances, it is generally advisable to focus on applying the principles of good occupational hygiene and take all practicable measures to prevent or control exposure in accordance with Section 4.6.**

Where exposure measurements are undertaken the results should inform the implementation of the risk management measures as suggested in the following Section.

**22** IFA (2009): Criteria for assessment of the effectiveness of protective measures, Institut für Arbeitsschutz der Deutschen Gesetzlichen Unfall versicherung (IFA), available from the IFA Internet site http://www.dguv.de/ifa/en

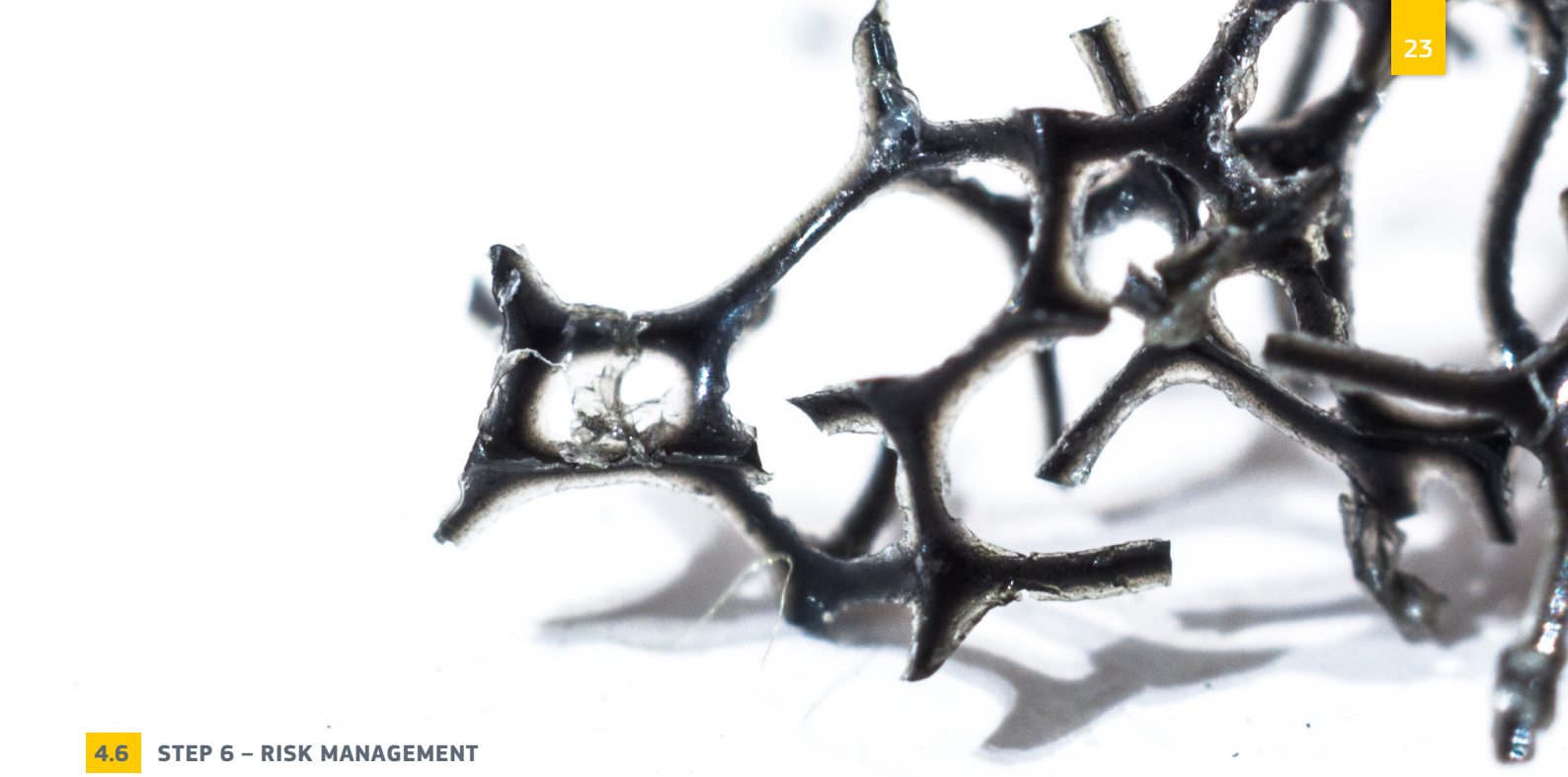
**23** See FNV, VNO, NCW,CNV (2011) Guidance working safely with nanomaterials and products, the guide for employers and employees, published by Dutch Ministry of Social Affairs and Employment.

**24** Pauluhn J (2009): Multi-walled Carbon Nanotubes (Baytubes®): Approach for Derivation of Occupational Exposure Limit, Regulatory Toxicology and Pharmacology, DOI: 10.1016/j.yrtph.2009.12.012

**25** NIOSH (2013): Occupational Exposure to Carbon Nanotubes and Nanofibers, Current Intelligence Bulletin 65, Department of Helath and Human Services, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health.

**26** Stone V et al (2009): ENRHES 2009, Engineered Nanoparticles: Review of Health and Environmental Safety, Edinburgh Napier University. Available at: https://www.nanowerk.com/nanotechnology/reports/reportpdf/report133.pdf

**27** NIOSH 2011, Occupational Exposure to Titanium Dioxide, Current Intelligence Bulletin 63, April 2011. http://www.cdc.gov/niosh/docs/2011-160/pdfs/2011-160.pdf



## 4.6 STEP 6 – RISK MANAGEMENT

### 4.6.1 GENERAL PRINCIPLES, HIERARCHY OF CONTROLS AND RISK MANAGEMENT MEASURES

Some national guidances have evaluated and recommended Risk Management Measures (see annex II).

The general principles for preventing risks associated with hazardous chemical agents are set out in articles 6(1) and (2) of Occupational Health and Safety Framework Directive 89/391/EEC and in article 5 of the CAD (reported in Box 2) can also be fully applied to the risk management of MNMs. Currently, the identified risk of MNMs depends on the hazardous properties of the MNM combined with the possibility of inhalation by workers. When the MNMs used or handled within the workplace cannot be substituted with other less hazardous chemical agents or be provided in a different form which is not subject to inhalation (e.g. pellets), the risk must be reduced by applying prevention or protection measures. A simple strategy is, for example, handling MNMs in liquid media or binding them in solid media.

"Applying these principles involves integrating the basic aspects of prevention into the work organisation and, in general, using logic and common sense in work involving hazardous chemical agents" (EC, 2004). Their applicability to MNMs is further explained below in box 2.

**Box 2 General principles for prevention of risks associated with hazardous chemical agents (article 5 of the CAD)**

Risks to the health and safety of workers at work involving hazardous chemical agents shall be eliminated or reduced to a minimum by:

- The design and organisation of systems of work at the workplace,
- The provision of suitable equipment for work with chemical agents and maintenance procedures which ensure the health and safety of workers at work,
- Reducing to a minimum the number of workers exposed or likely to be exposed,
- Reducing to a minimum the duration and intensity of exposure,
- Appropriate hygiene measures, reducing the quantity of chemical agents present at the workplace to the minimum required for the type of work concerned,
- Suitable working procedures including arrangements for the safe handling, storage and transport within the workplace of hazardous chemical agents and waste containing such chemical agents.

In applying the principles, the well-established hierarchy of controls (presented in Table 4.10) should be followed. A suitable combination of the risk control measures suggested in the following paragraphs should be adopted by employers to ensure the safe handling of MNMs.

**Table 4.10: Hierarchy of Controls**

| | |
|---|---|
| **Eliminate / Substitute** | The risks posed by a MNM can be eliminated by either avoiding its use or replacing it by a less hazardous agent, taking account of its conditions of use<br><br>MNMs (or its bulk form) which are classified as carcinogens or mutagens should be considered as a priority for substitution |
| **Modify process** | Change the process to reduce the extent of concern by, for example:<br>• Handling MNMs in liquid media or binding MNMs in solid media<br>• Reducing the amount of MNMs handled, on any given occasion or changing work procedures so as to minimise the exposure |
| **Isolate or Enclose** | All operations which involve the likely release of MNMs into the air are performed in contained installations or in facilities that can be operated remotely from a protected area |
| **Engineering Control** | All processes where there is the potential for creating dusts or aerosols of MNMs are carried out in areas with efficient local exhaust ventilation. Wet cutting is recommended for cutting solid articles containing MNMs |
| **Administrative Control** | Working procedures are developed for the safe handling of MNMs and job rotation programmes to minimise individual exposure are implemented. Workers potentially exposed to MNMs are consulted and informed about the results of the Risk Assessment and training courses about the control measures implemented are provided. An Emergency Management Plan should be established |
| **Personal Protective Equipment (PPE)** | PPE is a last resort control measure or a supplemental option to help support higher levels of exposure control. PPE may include respiratory protection devices, dermal protection and eye protection |

**Design and organisation of systems of work**

In designing the work processes, risks arising from the handling of dry ultrafine particles should be considered along with technological and economic aspects.

**Provision of suitable equipment for work with MNMs and maintenance procedures which ensure the health and safety of workers at work**

All workplaces must comply with the minimum ventilation requirements laid down in Directive 89/654/EEC, more precisely:

> *"5. Ventilation of enclosed workplaces*
>
> *5.1. Steps shall be taken to see to it that there is sufficient fresh air in enclosed workplaces, having regard to the working methods used and the physical demands placed on the workers. If a forced ventilation system is used, it shall be maintained in working order.*
>
> *Any breakdown must be indicated by a control system where this is necessary for workers' health.*
>
> *5.2. If air-conditioning or mechanical ventilation installations are used, they must operate in such a way that workers are not exposed to draughts which cause discomfort.*
>
> *Any deposit or dirt likely to create an immediate danger to the health of workers by polluting the atmosphere must be removed without delay".*

The aim in designing ventilation controls should be to ensure adequate control of the point of exposure for all work activities which involve risk of exposure to free nanoparticles, including packing for disposal.

The appropriateness of enclosure filtration systems will vary depending on the nature of the nanomaterial being handled. Thus, for CNTs and HARNs which show biopersistence, exhaust air should be filtered using a HEPA filter class H14. However, ductless HEPA-filtered safety cabinets and HEPA-filtered microbiological safety cabinets may be adequate for procedures involving only small quantities (e.g. <1 gram of CNTs). For nanomaterials which do not pose a specific health hazard, HEPA filters of at least H13 should be used. However, other hood types (e.g. capturing, receiving hoods or down draught benches) may be suitable for cutting, sawing or polishing of composite nanomaterials. Where enclosure is impractical, Local Extraction Ventilation (LEV) systems should be designed to enclose the process as much as possible.

Moreover, it is important to give careful consideration to the nature of any personal protective equipment (PPE) employed. For many nanomaterials, it will be acceptable to use laboratory coats or coveralls made from polyester/cotton or cotton in situations where exposure may occur. Where the clothing is intended to be reusable, there is an additional need to

consider what laundering practices are appropriate. In particular, washing outside the work premises should not be allowed in order to preclude risk of secondary exposure.

However, for high concern MNMs, it is recommended to use protective clothing made of materials such as polyethylene textiles since there is evidence suggesting that these MNMs may permeate through some intact disposable overall materials and, by implication, could pass through woven reusable materials. For the high concern MNMs, the use of wool, cotton, poly-cotton or knitted materials is not recommended.

When selecting gloves, it should be noted that material thickness is a major determinant of the protection provided. However, it is also essential to consider what other substances (e.g. solvents) may be present within the workplace environment. If it appears that latex is the safest choice, it is important to only use low-protein powder-free gloves. Although for some nanomaterials, use of suitable disposable single-use gloves manufactured to an appropriate standard may be acceptable. In the case of high concern MNMs, it is recommended that at least two layers of gloves are worn.

The use of eye protection is also recommended. As a minimum, close fitting safety glasses should be used for all nanomaterials.

Respiratory protective equipment should only be used when all other reasonably practicable measures have been taken but have not, in themselves, achieved an adequate level of control. If used with other measures (i.e. as a secondary precaution), disposable and half-masks should have an appropriate assigned protection factor (APF). If a high performance mask is going to be worn for long periods, the use of powered air flow designs should be considered. All workers required to wear RPE should undergo face-piece fit testing and training to ensure correct fitting and proper use.

**Reducing to a minimum the number of workers exposed or likely to be exposed**

This organisational measure aims to lower the collective risk involved in working with MNMs. However, it does not lower the individual risk. Work activities can be organised in order to minimise the number of workers exposed to MNMs by segregating the work areas from the rest of the workplace and restricting access to those areas.

**Reducing to a minimum the duration and intensity of exposure**

In working with MNMs, particular care should be taken to minimise inhalation. This can be achieved in two ways: by lowering the environmental concentration (e.g. through the installation of ventilation systems) and by minimising the exposure time to MNMs. Often, exposure can be lowered by acting cautiously when performing simple routine manual operations, such as opening bags, cleaning equipment by compressed air, etc.

**Appropriate hygiene measures**

It is particularly important that a high level of cleanliness is maintained in a workplace where nanomaterials are present since their small size enables them to enter easily and spread through the air where, depending on their tendency to form agglomerates, they may remain for considerable periods. For example, airborne non-agglomerated nanoparticles will behave much like gases and show

rapid diffusion over long distances as well as very slow sedimentation rates. For this reason, engineering and operational control systems should seek to limit opportunities for emission or accumulation of airborne nanoparticles in the work environment. In addition, if a spillage of nanomaterials occurs, it is important NOT to use a brush, compressed air or a standard vacuum cleaner for cleaning up. Removal should be achieved through use of a commercial HEPA-filtered vacuum cleaner dedicated to this purpose alone. The filter should be regularly changed under controlled conditions to ensure containment of the contents, which should be disposed of as hazardous waste. The vacuum cleaner itself will also need to be treated as hazardous waste at the end of its life cycle. Lastly, the area of spillage and any potentially contaminated equipment should be subject to wet-wiping.

**Reducing the quantity of MNMs present at the workplace to the minimum required for the type of work concerned**

Minimising the quantity of MNMs used or handled in each work activity leads to an efficient reduction of the intensity of exposure and, consequently, of the magnitude of the risk.

**Suitable working procedures including arrangements for cleaning and maintenance operations and for the safe handling, storage and transport within the workplace of MNMs and waste containing MNMs**

Cleaning of work premises and maintenance of machinery used for the processing of MNMs should be carried out by trained workers with suitable personal protective equipment. Wet cleaning or the use of an industrial vacuum cleaner for dust class H is advised. When cleaning, applying a strong jet of water should be avoided, in order to minimise the possibility of suspension of dust. Cleaning with compressed air should be avoided.

The correct design of the working procedures can prevent unnecessary exposure. The handling, storage and transport of MNMs should be carried out by trained workers only.

Moreover, disposal of waste contaminated with nanomaterials should adopt a precautionary approach, unless there are known to be no potential hazards or concerns posed by the material. Otherwise, the waste should be double-bagged or doubly-contained in labelled and sealed containers and disposed of as hazardous waste (preferably using incineration).

**Emergency procedures in case of accidental release**

In the event of a spillage of dry nanopowders or in any extraordinary situations that might result in a high exposure to MNMs, all the persons in the work premises should be evacuated. The accident zone should be restricted and re-entered only once the MNMs have settled; since a certain load of airborne MNMs should be expected in any case, suitable PPE (such as a dust-proof suit type 5, gloves and respirator with P3 filter) should be worn during the cleaning operation.

Table 4.11 (at the end of this Section) can be used for recording the RMMs to be implemented.

### 4.6.2 RISK LEVEL 1

In general, in these situations, the risk to the health and safety of workers may be regarded as slight within the meaning of Article 5(4) of the CAD. In addition, if the application of the general principles for prevention is sufficient to reduce this risk, Article 5(4) of the Directive establishes that the provisions of Articles 6, 7 and 10 do not need to be applied. Normally, **such situations can be controlled through the use of general ventilation.**

### 4.6.3 RISK LEVEL 2

**In the following situations,** specific prevention measures should be implemented, in addition to what is required for risk level 1 situations:

- Where the emission of medium-high concern MNMs is anticipated as very low or unlikely;
- Where the emission of medium-low concern MNMs is probable or very low;
- Where low concern MNMs are likely to be emitted.

For risk level 2, engineering control measures such as local extraction might suffice in minimising the exposure and associated risk.

In situations leading to a risk level 2 according to table 4.7, **specific prevention measures should be implemented,** in addition to what is required for risk level 1 situations. Engineering control measures such as local exhaust ventilation might suffice in minimising the exposure and associated risk.

### 4.6.4 RISK LEVEL 3

In the following situations, **closed systems or containment must be used. A detailed Risk Assessment, informed by exposure measurements, should be carried out with the assistance of an expert:**

- Where MNMs of high concern are used but their emission is expected to be very low;
- Where the emission of MNMs of medium-high concern is probable due to their dustiness and the characteristics of the work activities;
- Where poorly soluble/insoluble nanomaterials with no specific toxicity are likely to be emitted.

The optimum combination of engineering control measures, administrative control measures and the adoption of personal protective equipment by the workers potentially exposed to the MNMs should be selected and implemented to minimise exposure.

In situations leading to a risk level 3 according to table 4.7, **closed systems or containment must be used** and their efficiency ensured by checking regularly their performance (this may be done by measuring key variables of the functioning of the control systems and/or by measuring airborne concentrations of the MNM).

### 4.6.5 RISK LEVEL 4

In the following situations, **it is essential that measures specifically designed for the processes in question are adopted:**

- where MNMs have given rise to significant concerns over their potential impacts on human health on the basis of the evidence gathered by research (namely poorly soluble/insoluble WHO nanofibres) and where it is likely or probable that emissions will occur during the work activities resulting in a high level of exposure of the workers; and / or

- where MNMs have given rise to a medium-high concern (namely poorly soluble/insoluble nanoparticles with specific toxicity and poorly soluble/insoluble HARNs other than those encompassed in concern category 1) and the MNMs easily could be released into the atmosphere.

In situations leading to a risk level 4 according to table 4.7, **it is essential that measures specifically designed for the processes are adopted.**

Measurements within the facilities should be carried out in order to quantitatively evaluate exposures. Although **Occupational Exposure Limits for nanomaterials have not been established yet,** for a few specific MNMs industry and research have suggested either specific OELs or DNELs. Such values might be used by employers as thresholds over which additional RMMs should be implemented. A detailed Risk Assessment (as for Section 4.5) and periodic exposure measurements should be carried out in order to determine which RMMs need to be implemented and to verify their effectiveness.

As a reminder and according to table 4.10, when the application of the Control Banding results in Risk level 4, according to the hierarchy of control, employers should consider as a first step the possibility of substituting the MNM (following an approach similar to that set out in the CMD for carcinogens and mutagens in the workplace). If substitution is not possible, employers should consider how to modify processes in order to minimise the potential emission of nanoparticles, e.g. avoiding working with dry nanopowders (dispersing the MNM in liquid media, binding it into solid matrices or, if the MNM is already in a liquid, avoiding procedures that might lead to the formation of aerosols).
If substitution/modification of working procedures is not possible or not sufficient for the reduction of MNM emissions, employers should consider containment of those working procedures and the design / introduction of closed systems.

If containment is technically not possible, consider the instalment of suitable engineering control equipment, the adoption of administrative control measures and the provision of suitable personal protective equipment, as presented in the previous subsection.

### 4.6.6 INFORMATION, INSTRUCTION AND TRAINING

Particular attention should be given to training all employees who may be exposed to nanomaterials, so that they understand the potential health concerns regarding these materials as well as the importance of taking all necessary precautions to avoid or minimise exposure. This training should include clear explanation of what control measures should be used for particular work activities or in particular parts of the workplace. In addition, each employee should be aware of his/her responsibility to report any defects or weaknesses in the control measures. Workers should also be encouraged to report any problems and to suggest improvements. Employers should also provide adequate supervision, particularly to new or inexperienced workers.

As a minimum, training on the safe handling of nanomaterials should include instruction on:

- The risks in relation to physicochemical hazards (e.g. fire and explosion);

- The potential nature of health concerns;

- The proper use of protective equipment (e.g. wearing appropriate personal protection equipment before handling nanomaterials) and the need to maintain such equipment; and

- The need to comply with all operational procedures enacted to ensure protection.

The selection of appropriate hazard labelling and pictograms should be informed by an understanding of the potential hazard posed by the nanomaterials used in the workplace. In the absence of definitive information, a precautionary approach is recommended. However, currently there is no EU-wide recognised workplace sign/pictogram that advises specifically on the presence of nanomaterials. Nonetheless, some organisations have developed unofficial pictograms intended to denote the presence of nanomaterials, for example, in relation to the use of a yellow warning triangle format. The use of clearly understandable pictograms may provide a visual indication of the presence of nanomaterials. Irrespective of considerations to employ such unofficial pictograms, it is important to ensure that all appropriate official risk and safety phrases and warning pictograms are in place and that the workforce has access to all relevant information on actual or potential hazards or safety risks.

### 4.6.7 HEALTH SURVEILLANCE

Article 2(f) of CAD defines the basis for monitoring the state of health of individual workers if they are exposed to specific chemical agents. Article 10 mandates the use of such monitoring where the following conditions are simultaneously met:

- the worker's exposure to a hazardous chemical agent is such that an identifiable disease or adverse effect on health may be associated with that exposure;
- there is a likelihood that the disease or effect may occur under the conditions of the worker's work; and
- the surveillance technique is such as to be of low risk to the worker.

The actual nature of the health surveillance that should be undertaken is defined on the basis of the risk assessment (Article 4) and will thus vary depending on the nature of the MNM to which the worker is exposed. Various techniques may be employed including: the conduct of medical examination, use of health questionnaires or interviews, or clinical pathology investigation.

In the case of MNMs, current scientific uncertainty has given rise to concerns that their physicochemical properties may pose a risk to worker health which, as yet, is poorly characterised. Hence, it is debatable whether, based on current knowledge, specific medical surveillance investigations are appropriate for potentially exposed workers.

The health surveillance undertaken should reflect the national practices and requirements. At a minimum, it is suggested that records are kept of all those working with nanomaterials, as would be the case for other substances of concern.

## 4.7 STEP 7 – REVIEW

The risk assessment and the efficacy of the implemented risk management measures must be reviewed periodically and before any changes in the chemical agents or working conditions (in compliance with CAD Article 4(5)). However, the review process is subject to the same limitations of detailed risk assessment.

**Table 4.11 Risk Management plan**

| Tasks | MNM | MNM Physical state | Control Band | Engineering Controls | Administrative and PPE Controls | Officer responsible for implementation | Planned date for measure being in operation |
|---|---|---|---|---|---|---|---|
| Material Receipt, Unpacking and Delivery | | | | | | | |
| Laboratory Operations | | | | | | | |
| Manufacturing and Finishing | | | | | | | |
| Cleaning and Maintenance | | | | | | | |
| Storage, Packaging and Shipping | | | | | | | |
| Waste Management | | | | | | | |
| Reasonable Foreseen Emergencies | | | | | | | |
| Other | | | | | | | |

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- **Hansen et al (2011):** NanoRiskCat – A Conceptual Decision Support Tool for Nanomaterials, Environmental Project No. 1372/2011, Danish Ministry of the Environment, Environmental Protection Agency.
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- **HSE (2013):** Using nanomaterials at work, Including carbon nanotubes (CNTs) and other biopersistent high aspect ratio nanomaterials (HARNs). Health and Safety Executive, UK.
- **HSE (2011):** EH40/2005 Workplace exposure limits containing the list of workplace exposure limits for use with the Control of Substances Hazardous to Health Regulations (as amended), Crown copyright.
- **INRS (2012):** Valeurs limites d'exposition professionnelle aux agents chimiques en France, ED 984 Aide-Mémoire Technique. IVAM UvA et al (2011): Guidance working safely with nanomaterials and –products, the guide for employers and employees, prepared for the Dutch Ministry of Social Affairs and Employment.
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- **RPA et al (2013):** Assessing the Suitability of the Current EU Legal Framework for Ensuring the Health and Safety of Workers from Nanomaterials in the Workplace, prepared for the European Commission DG Employment, Social Affairs and Equal Opportunities.
- **RPA et al (2011):** Occupational Safety and Health and the Chemical Classification, Labelling and Packaging Regulation, Guidance to help employers and workers to manage the transition to the new system, prepared for DG Employment, social affairs and equal opportunities. Available at: https://osha.europa.eu/en/themes/dangerous-substances
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# Annex I – Concerns over Hazards and Risks of Nanomaterials

## WHY DO MNMS NEED TO BE TREATED AS SPECIAL CASE?

The reason why MNMs are of such interest and offer such potentially significant benefits to society is that they often have very different properties to the same substances on the macro scale – they may be more reactive, have increased strength, etc. However, these same differences also mean that they may also be more readily absorbed into biological systems and that their hazards may be different from those of their larger forms.

"From a toxicological point of view nanomaterials of poor solubility in biological fluids are of special importance, because they maintain their nanostructure after contact with the human body. Nanomaterials that are enclosed in an insoluble matrix are of minor importance, but may become relevant as soon as they are released by e.g. mechanical forces". It should be noted that "most of currently relevant nanomaterials occur in a solid aggregate state and have a (very) low solubility" (EU-OSHA, 2009).

## CONCERNS OVER THE POSSIBLE HAZARDS OF NANOMATERIALS

Although the potential effects of nanomaterials on human health can vary from those of the chemical agents in macro-forms due to their specific physicochemical characteristics, the possible mechanisms for the generation of harm remain the same: the causation can be direct, through contact, or indirect, through the production of some form of energy which can have an adverse effect on human health. In the first case, exposure might result in an "acute effect", when the harm becomes apparent rapidly or even immediately after contact, or in a "chronic effect", when the harm appears in the long term, normally due to repeated exposure over time. Moreover, the term "local effect" is used if the harm becomes apparent at the point of contact; "systematic effect" denotes harm that appears in any point of the body regardless of the place where the contact occurred, normally following a process of absorption and distribution through the body (EC, 2004). "The smallness of nanomaterials can lead to an increased potential to cross barriers in living organisms which increases the number of organs that can be affected" (EU-OSHA, 2009). Nanomaterials could also cause harm by fire or explosion.

Extensive research campaigns are being conducted for the understanding of the possible hazards of nanomaterials; "Not all nanomaterials are hazardous, not all nanomaterials are equally hazardous and there can be considerable variation in toxicity between nanomaterials with a similar chemical composition, because of their physicochemical characteristics" (HSE, 2013). This section summarises the findings of the literature review on the workplace exposure to nanoparticles (EU-OSHA, 2009) commissioned by the European Agency for Safety and Health at Work and conducted by members of different OSH national institutes, namely:

- Bundesanstalt für Arbeitsschutz und Arbeitsmedizin (BAuA, project leader), Germany;
- Institut National de Recherche et de Sécurité pour la prévention des accidents du travail et des maladies professionnelles (INRS), France;
- Centralny Instytut Ochrony Pracy - Państwowy Instytut Badawczy (CIOP-PIB), Poland;
- Instituto Nacional de Seguridad e Higiene en el Trabajo (INSHT), Spain.

Methods for the assessment of health effects are usually divided in four groups:

- Epidemiology/occupational medicine;
- In vivo methods with animals;
- In vitro methods;
- Methods for the determination of physicochemical properties.

The OECD Working Party on Manufactured Nanomaterials (WPMN) is scrutinising the adequacy of the current test guidelines to deliver results for hazard classification of nanomaterials and is preparing new standardised testing procedures with a particular care on the sample preparation and dosimetry.

## CONCERNS OVER PHYSICAL HAZARDS

There is a wide consensus on the lack of knowledge and the need for further research on the safety risks that might be posed by nanopowders.

When handling nanopowders, particular attention should be paid to the catalytic effects and the risk of fire or explosion. Moreover, in some specific work activities, other possible hazards should be considered, for example:

- During the generation of a plasma via the use of high currents, hazard of electrocution might be increased;
- During work activities with possible leaks of inert protective gases there might be an asphyxiation hazard.

Due to their greater surface area, nanoparticles can be easily charged electrostatically, thus increasing the risk of ignition and the violence of an explosion. Furthermore, due to their size, they might remain airborne for long periods of time, thus increasing the possibility of creating potentially explosive dust clouds.

The Nanosafe2 project[28] ranked various carbon black powders, aluminium nanoparticles of different sizes and carbon nanotubes in terms of their flammability and explosivity: on a scale from 0 to 3, where 0 is "no explosion", 1 corresponds to "weak explosion", 2 to "strong explosion" and 3 to "very strong explosion", carbon black and carbon nanotubes are in the dust explosion class 1 "weak explosion", while aluminium nanopowders, depending on the particle size, were ranked in the highest classes 2 and 3, from "strong explosion" to "very strong explosion".

**28** http://www.nanosafe.org/cea-tech/pns/nanosafe/en

### CONCERNS OVER HEALTH HAZARDS

Epidemiological studies were mainly conducted on the effects of carbon black, one the MNMs that has been used for many decades. However, the International Agency for Research on Cancer (IARC) evaluates carbon black as possibly carcinogenic to humans (Group 2B), as there is sufficient evidence in experimental animals but inadequate evidence in human epidemiological studies[29]. Moreover, it is not certain whether workers were exposed to carbon black at nanoscale or micro-scale. This same uncertainty also undermines epidemiological studies on nano-titanium dioxide.

**29** http://publications.iarc.fr/111

According to HEI (2013), a growing number of epidemiological studies have been conducted over the last ten – fifteen years on the human health effects of ultrafine particles (naturally-occurring nanoparticles). However, the evidence of adverse effects from short-term exposure to ambient UFPs on acute mortality and morbidity from respiratory and cardiovascular diseases is suggestive rather than conclusive. Due to underlying deficiencies in exposure data, it is not possible to conclude (or exclude) that UFPs alone account substantially for the adverse effects associated with other ambient pollutants such as $PM_{2.5}$. No epidemiological studies of long-term exposures to UFPs have been conducted so far.

Due to the uncertain reliability of in-vitro methods to assess the health effects of nanomaterials and the limited and inconclusive epidemiological evidence, in-vivo studies provide most of the data on which the current concerns have been built.

Short and mid-term duration animal studies have provided evidence of toxic effects to the lung (inflammation, cytotoxicity and tissue damage) of different types of MNMs (e.g. carbon black, titanium dioxide, carbon nanotubes, $C_{60}$-fullerenes and amorphous silicon dioxide). However, there is conflicting evidence on the higher potency of nanomaterials compared to micro-sized particles. Markers of inflammation in the brain were observed in rats following inhalation exposure to nano-manganese. Some preliminary studies detected effects similar to those of asbestos for specific modification of carbon nanotubes. Several types of nanomaterials have shown the capacity of systemic distribution in the organism; however, the toxicological implications of the availability of MNMs in further organs were not sufficiently classified.

Animal studies of long-term duration raised evidence on lung toxicity following inhalation exposure to nano-carbon black and nano-titanium dioxide and lung tumours were evoked in rats. The intratracheal instillation of different types of MNMs (namely carbon black, aluminium oxide, aluminium silicate, titanium dioxide, and amorphous silicon dioxide) has induced tumours and a higher potency of nanomaterials compared to micro sized particles have been observed. "However, there are insufficient data to confirm the health consequences of long-term repeated exposure" (HSE, 2013).

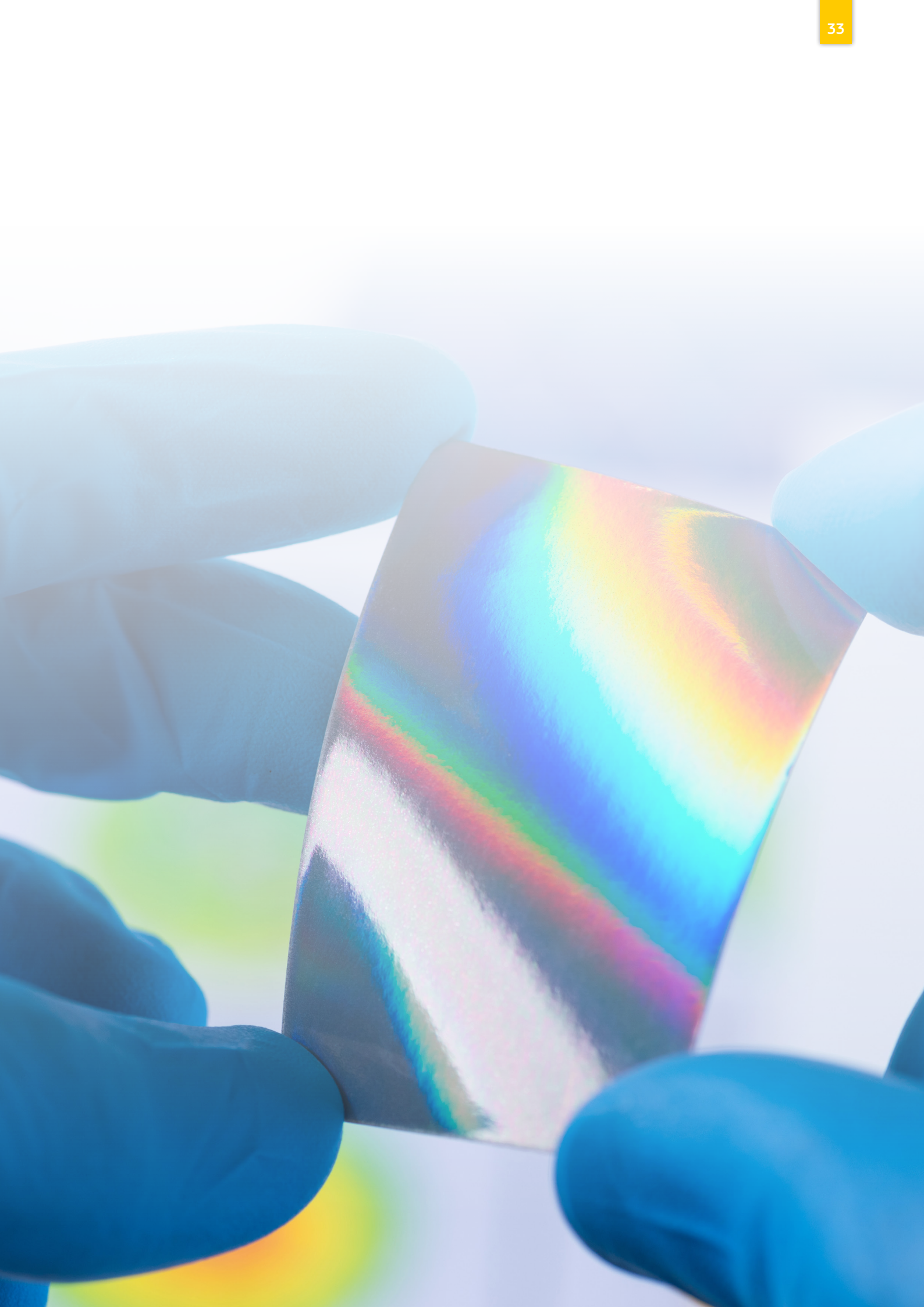
The US National Institute for Occupational Safety and Health (NIOSH) has determined, in light of the results of in-vivo studies, that exposure to ultrafine $TiO_2$ should be considered a potential occupational carcinogen, acting "through a secondary genotoxicity mechanism that is not specific to $TiO_2$ but primarily related to particle size and surface area". Moreover, "the higher mass-based potency of ultrafine $TiO_2$ compared to micro sized $TiO_2$ is associated with the greater surface area of ultrafine particles for a given mass". This has led to the setting of different Recommended airborne Exposure Limits of 2.4 mg/m$^3$ for fine (micro sized) $TiO_2$ and 0.3 mg/m$^3$ for ultrafine (nano sized) $TiO_2$ (including manufactured nano-$TiO_2$), as time-weighted average (TWA) concentrations for up to 10 hours per day during a 40-hour work week. Importantly, NIOSH concluded that the adverse effects of inhaling $TiO_2$ may not be material-specific but appear to be due to a generic effect of poorly soluble low-toxicity (PSLT) particles in the lungs at sufficiently high exposure. While NIOSH concludes that there is insufficient evidence to classify fine $TiO_2$ as a potential occupational carcinogen, NIOSH is concerned about the potential carcinogenicity of ultrafine and engineered nanoscale $TiO_2$ if workers are exposed at the current mass-based exposure limits for respirable or total mass fractions of $TiO_2$. NIOSH recommends controlling exposures as low as possible, below the RELs" (NIOSH, 2011).

## Annex II – Further Guidance on the Use of Nanomaterials

Readers are advised that, while the following guidance materials may be considered to be representative of the documents available at the time of collation, this listing should be viewed as not exhaustive. Also, in some cases the approaches suggested by the guidance documents may not be compatible or consistent and their inclusion in this listing should not be regarded as suggesting they necessarily constitute 'best practice' within the context of the European Union. It should appreciated also that the development of understanding in relation to the health and safety issues relating to the manufacture and use in industry of nanomaterials is a rapidly developing area and that revised or additional guidance materials are frequently being published by various bodies. Therefore, users are advised to check for the latest available information that may be available, rather than rely on the sources identified below.

In addition to the listed sources, it should be the International Organization for Standardization (ISO) publishes a series of standards and guidance materials (available to purchase; topics may be viewed via Internet site: http://www.iso.org/iso/home.html).

Furthermore, the Organisation for Economic Co-operation and Development (OECD) also publish on the topic of the safe use of nanomaterials in the workplace (the latest versions are freely accessible via Internet site: http://www.oecd.org/chemicalsafety/nanosafety/publications-series-safety-manufactured-nanomaterials.htm



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- **AUVA (undated):** Merkblatt M 310 Nanotechnologien - Arbeits- und Gesundheitsschutz. Allgemeine Unfallversicherungsanstalt, Austria. Available at Internet site: https://www.auva.at/cdscontent/load?contentid=10008.544597&version=1430386826
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## Denmark

- **Depa (2011):** NanoRiskCat (NRC) - A Conceptual Decision Support Tool for Nanomaterials. Danish Environmental Protection Agency (DEPA), Denmark. Available at Internet site: https://www2.mst.dk/udgiv/publications/2011/12/978-87-92779-11-3.pdf

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## Germany

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## Annex III – Examples of applications of MNMs

**Table III-a: Main Application Areas of nanomaterials**

| MNM | Main Application Areas |
|---|---|
| **Nano-silver** | Nano-silver is currently the most commonly used nano-object in a wide range of consumer products. It is used in cosmetics and personal care products, food and health-food, antimicrobial paints and coatings, hygienic surfaces and packaging materials, medical applications etc. |
| **Carbon black** | Carbon black has been produced at industrial scale in high tonnage volumes for many years, and has many applications including tyre manufacturing and dye/pigment manufacture. |
| **Carbon nanotubes** | Because of the high tensile strength, the main use of CNTs is in structural materials, such as ceramic and polymer composites, conducting composites for the aerospace, automotive and electronics industries, and in adhesives such as epoxy resin. A major area of CNT application is in the electronics sector. |
| **Fumed (amorphous) silica** | Fumed amorphous silica has been produced in high tonnage volumes for many years, and is widely used for a variety of applications. These include paints and coatings, polishing microelectronic devices, food contact surfaces and food packaging applications. Porous silica is also used in nano-filtration of water and beverages. Amorphous silica is believed to be used in food applications, such as in clearing of beers and wines, and as a free flowing agent in powdered soups (and in condiments). |
| **Nano-titanium dioxide** | Nano-titanium dioxide is produced in high tonnage volumes for main uses in paints and coatings (as a UV absorber to help prevent UV degradation), cosmetics (in sunscreens to prevent UV damage to skin), and packaging applications. |
| **Zinc oxide** | Zinc oxide is currently produced in small but growing tonnage volumes. It is mainly used in cosmetics and personal care products, but other applications such as antimicrobial packaging have also emerged recently. |
| **Nanoclays** | Nanoclays are used for a variety of applications. The nanoclay mineral most commonly used is montmorillonite (also termed as bentonite), which is a natural clay obtained from volcanic ash/rocks. Nanoclays have a natural nano-scaled layer structure and are often organically modified to bind to polymer matrices to develop improved materials, such as composites with enhanced gas-barrier properties for food packaging. |
| **Nano-cerium oxide** | Nano-sized cerium oxide is used as a secondary fuel catalyst in diesel. The application is claimed to reduce fuel consumption and particulate emissions. |
| **Nano-iron** | Zero-valent nano-iron is finding an increasing use in water treatment and for the remediation of contaminated soils. Nano-iron is used in the treatment of contaminated waters, e.g. groundwater, where it is claimed to decontaminate water by breaking down organic pollutants and killing microbial pathogens. |

**Table III-a: Main Application Areas of nanomaterials**

| MNM | Main Application Areas |
|---|---|
| **Organic nanomaterials** | A wide range of organic nanomaterials is available, or under research and development (R&D), for uses mainly in cosmetics, food and medicine sectors. Examples of possible uses for organic nanotechnology include vitamins, antioxidants, colours, flavours, preservatives, active ingredients for cosmetics and therapeutics, detergents etc. The main tenet behind the development of nano-sized organic substances is the greater uptake, absorption and bioavailability of bioactive substances in the body, compared to conventional bulk equivalents. |
| **Other** | Other nanomaterials that are produced at an increasing commercial scale include metal and metal oxides of aluminium, copper, tin, zirconium, metal nitrides (e.g. titanium nitride), alkaline earth metals (calcium, magnesium), non-metals (selenium).<br><br>Quantum dots – composed of metal (oxide), or semiconductor materials with novel electronic, optical, magnetic and catalytic properties are also finding increasing applications in medical imaging and diagnostics and security printing. The production of quantum dots, however, may not be high-tonnage at present. |

Source: Milieu & RPA (2010)

# Annex IV – Legislation Applicable to Nanomaterials

MNMs are not covered by specific regulations but rather are subject to the same EU and national legislation that ensures the safe handling of conventional chemicals and mixtures. There is a wide consensus that the Chemical Agents Directive 98/24/EC is the most relevant legislative act to comply with in order to ensure the safe handling of MNMs in the workplace.

It should be noted that nanomaterials are not explicitly included in or excluded from the scope of the Directive, but the "safeguard" subpara (Art. 2(b)(iii)) makes it clear that the general objective covers them in principle and the CAD applies provided that the hazard is known.

The key aspect is indeed the identification of the hazard. While it is true that "hazard identification" is the first step of a risk assessment, nevertheless the identification of a "chemical hazard" (where the identification of a hazard potentially posed by NMs requires a similar level of knowledge) partially relies on information passed by the supplier of the substances or mixtures through the safety data sheets accompanying them. However, the lack of safety data sheets accompanying MNMs or the lack of specific information on MNMs in the safety data sheet of the bulk form of the material does not mean that MNMs cannot be identified or regarded as hazardous: as explained by the Practical Guidelines developed by the European Commission to comply with Art. 12(2) of the CAD : "chemical agents in the workplace may pose risks to the health or safety of workers on account of: (...) the manner in which they are present in the workplace (e.g.: inert solid in the form of a breathable powder)" (EC, 2004, p.13).

Moreover, in paragraph 1.1.2, the same document explains that "...any substance which has an exposure limit value must be regarded as a hazardous substance. This is the case with particles of insoluble materials which are not classifiable as dangerous to health".

At the pan-European level, currently there are no general exposure limits for dusts; only certain OELs referring to specific substance dusts. However, in many Member States there are general (default) limit values for dusts based on respirable or inhalable size criteria. As illustrative examples:

- In France[30] , les Valeurs limites d'exposition professionnelle are set at 10 mg/m³ for the inhalable fraction and 5 mg/m³ for the respirable fraction.
- In Germany[31] , allgemeiner Staubgrenzwert (general dust limit values) have been set up for alveolengängige Fraktion (respirable fraction) at 3 mg/m³ and for einatembare fraction (inhalable fraction) at 10 mg/m³;
- In the UK[32] , the COSHH definition of a substance hazardous to health includes dust of any kind when present at a concentration in air equal to or greater than 10 mg/m³ 8-hour TWA of inhalable dust or 4 mg/m³ 8-hour TWA of respirable dust;

Consequently, whenever nanomaterials are present in the workplace, they are subject to the CAD provisions. In this case, the main obligations on employers are:

- To carry out risk assessments pertaining to chemical agents and their related risks. These should be carried out by obtaining the necessary "additional information [...] from the supplier or from other readily available sources". These risk assessments need to be documented and kept up-to-date (Article 4);
- To prevent chemical risk, meaning that such risks are "eliminated or reduced to a minimum". The ways in which this should be achieved are laid out in Articles 5 and 6 and consist of, in order of priority:

**30** INRS (2012): Valeurs limites d'exposition professionnelle aux agents chimiques en France, ED 984 Aide-Mémoire Technique.

**31** BAuA (2012): TRGS 900 – Technische Regeln für Gefahrstoffe – Arbeitsplatzgrenzwerte, GMBl 2012 S. 715-716 Nr.40.

**32** HSE (2011): EH40/2005 Workplace exposure limits containing the list of workplace exposure limits for use with the Control of Substances Hazardous to Health Regulations (as amended), Crown copyright.

- Substituting hazardous agents or processes by less hazardous ones;
- Designing work processes and controls to eliminate or minimise the release of hazardous chemical agents;
- Applying collective protection measures (e.g. ventilation);
- Applying personal protection measures;

- To have emergency provisions in place to deal with accidents, incidents and emergencies (Article 7); and

- To provide information and training for workers pertaining to the results of the risk assessment carried out; the identity, risks and occupational exposure limit values and legislative provisions of the chemical agents used in their workplace; and the appropriate precautions and actions to be taken (Article 8).

The CAD also re-states the OSHD obligation of employers to provide for "consultation and participation of workers and/or their representatives [...] on the matters covered by this Directive". In addition to the above, there are prohibitions on four chemical agents listed in Annex III.

A non-exhaustive list of acts and regulations supplementing the CAD which apply within the European Union is provided below:

- Council Directive 89/391/EEC of 12 June 1989 on the introduction of measures to encourage improvements in the safety and health of workers at work;

- The ATEX Directive 99/92/EC (also known as 'ATEX 137' or the 'ATEX Workplace Directive') - requires employers to meet requirements for the protection of workers potentially at risk from explosive atmospheres;

- Directive 2004/37/EC of the European Parliament and of the Council of 29 April 2004 on the protection of workers from the risks related to exposure to carcinogens or mutagens at work (Sixth individual Directive within the meaning of Article 16(1) of Council Directive 89/391/EEC) (codified version) (Text with EEA relevance);

- Council Directive 92/85/EEC of 19 October 1992 on the introduction of measures to encourage improvements in the safety and health at work of pregnant workers and workers who have recently given birth or are breastfeeding (tenth individual Directive within the meaning of Article 16 (1) of Directive 89/391/EEC);

- Council Directive 94/33/EC of 22 June 1994 on the protection of young people at work;

- Council Directive 89/656/EEC of 30 November 1989 on the minimum health and safety requirements for the use by workers of personal protective equipment at the workplace (third individual directive within the meaning of Article 16 (1) of Directive 89/391/EEC).

All of these worker protection laws require that employers identify hazards and carry out a risk assessment so that the potential risks identified can be eliminated or reduced as far as is practicable.

Other regulations which apply to chemicals placed on the market include:

- The REACH Regulation (EC) No 1907/2006 – requiring manufacturers and importers to gather information on the properties of their chemical substances which will allow their safe handling. When reviewing data provided as part of a registration under REACH, one should be aware that in many cases much of the data provided in the registration dossier will have been generated for the bulk form of the substance. As previously mentioned, it is duty of the supplier (according to Articles 31 and 32 of the REACH Regulation) to communicate down the supply chain "any other available and relevant information about the substance that is necessary to enable appropriate risk management measures to be identified and applied including specific conditions resulting from the application of Section 3 of Annex XI" (Art. 32(1)(d)). Subsequently, any downstream user, in order to comply with the CAD and carry out a risk assessment to identify the appropriate RMMs, can ask for further information (free of charge[33]) of the supplier about, at least, the size of the particles of the substance/mixture and its solubility/biopersistence characteristics, since comprehensive toxicological research has shown without any reasonable doubt that the inhalation of any biopersistent/poorly soluble particles can have harmful effects on the respiratory system;

- The CLP Regulation (EC) No 1272/2008 - requires that chemical substances and mixtures placed on the market are appropriately classified for their possible hazardous effects and labelled and packaged accordingly. In light of Articles 5(1), 6(1), 8(1)(2)(6) and 9(5), "manufacturers, importers and downstream users shall consider the forms or physical states in which the substance or mixture is placed on the market and in which it can be reasonably expected to be used". Companies are expected to make use of the relevant available information created, e.g. under REACH, and conduct additional testing where required for physicochemical properties. Tests should therefore be carried out on representative samples of the substance or mixture as it is placed on the market. As explained in EC (2009), "a substance with different particle sizes or forms can have different classifications, as is the case for e.g. nickel and nickel powder (particle diameter <1 mm). If substances are produced/imported both at nanoscale and as bulk, a separate classification and labelling may be required if the available data on the intrinsic properties indicates a difference in hazard class between the nanoform and ones the bulk form";
- The Cosmetics Regulation No 1223/2009 - requires that cosmetic products containing nanomaterials shall be notified to the Commission, providing physical and chemical properties of the

**33** Article 32(2) of the REACH Regulation.

nanomaterial, the quantity intended to be placed on the market, its toxicological profile, the safety data and the foreseeable exposure conditions. Furthermore, it requires all ingredients in the form of nanomaterials to be clearly labelled and followed by the word “nano”;

- The Biocides Regulation No 528/2012 - requires that, where nanomaterials are used in biocidal products, the risk to human health, animal health and the environment shall be assessed separately and the ingredients in nano-form clearly labelled as nanomaterials;
- The Food Information to Consumers Regulation No 1169/2011 - requires that all ingredients present in the form of MNMs shall be labelled as nanomaterials.

This Guidance document should be read in conjunction with the available guidance on complying with these regulations.

# Annex V – Challenges in Monitoring Exposure to Nanomaterials

The challenges in monitoring exposure to nanoparticles may be illustrated by the current lack of consensus as to what constitutes the most appropriate metric to describe MNM exposure. For bulk forms of substances, a mass-based measurement is generally employed (except in the case of fibres where a number-based metric is used); however, scientific evidence suggests that particle (or fibre) number or surface area based measures may be of more relevance when considering NMs. Consequently, the gravimetric measurement methods usually employed for airborne monitoring are not ideal, and so number-based methods are generally regarded as also being necessary. There exist a number of techniques and associated instrumentation which may be of value for establishing exposure levels for nanoparticles (see Table V-a). However, it should be emphasised that these have generally been developed for research applications, rather than routine workplace monitoring. Furthermore, it should be noted that the available measurements methods for NMs are susceptible to spatial and temporal variability and have yet to be validated at the EU level.

**Table V-a: Examples of monitoring instrumentation that may be applied for MNM exposure measurements**

| Device | Capable of measuring (metric) | Note |
|---|---|---|
| **Size-selective static sampler** | Mass | Cascade impactors can offer a cut point of 1 around 100 nm |
| **Size-selective personal sampler** | Mass | Subject to technical limitations and potentially complex analysis. Mass may also be derived by size-distribution measurements |
| **Tapered Element** | Mass | Sensitive and offering real-time monitoring |
| **SMPS** | Mass; Number; (Surface area) | Data output interpretable in terms of mass concentration and number concentration or, in some circumstances, surface area |
| **ELPI** | Mass; Number; Surface area | Offers real time monitoring. Data output interpretable in terms of mass concentration, number concentration or surface area |
| **CPC** | Number | Offers real time monitoring. Requires customisation to operate specifically at nano-range |
| **Optical Particle Counter** | Number | Limitations to particle size range they are suitable for |
| **Diffusion Charger** | Surface area | Offers real time monitoring. Not all instruments of this type are suitable and even then requires customisation |

*Source: Adapted from Aitken et al (2011)*

The situation is further complicated by the technical difficulties in attempting to differentiate between MNMs and background sources of nano-scale particles (which may be carried into the workplace in ambient air or generated as a result of processes undertaken within the workplace). In this respect, it should be appreciated that urban air typically contains between 10,000 to 40,000 particles per $cm^3$ while in industrial settings, additional nano or ultrafine-particles may arise from the operation of heating units, fork lift trucks, vacuum cleaners and as exhaust from engines, as well as process-related activities such as cutting, grinding and polishing. All these various sources will contribute to the total load in air of particles with diameters <100 nm. In this respect, where an air monitoring program is being considered, it may be helpful as a first step to measure the extent of nano-particulate dusts present in the workplace as 'background' pollutants before beginning MNM-based operations. This way, any results obtained with regard to MNMs can be placed into context against background exposures.

Further insights into the technical approaches to monitoring exposure to nano-forms and the associated challenges may be gained from a range of published sources, including:


- **Aitken et al. (2011):** Specific Advice on Exposure Assessment and Hazard/Risk Characterisation for Nanomaterials under REACH (RIP-oN 3) – Final Project Report. Document reference RNC/RIP-oN3/FPR/1/FINAL.
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