



**Safe handling of
nanomaterials and
other advanced materials
at workplaces**

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1 Abbreviations and acronyms

AGS	Ausschuss für Gefahrstoffe / German Committee on Hazardous Substances
ATEX	Atmosphère Explosive
AVV	Abfallverzeichnis-Verordnung / Verordnung über das Europäische Abfallverzeichnis / European listing of waste products
BAuA	Bundesanstalt für Arbeitsschutz und Arbeitsmedizin / Federal Institute for Occupational Safety and Health
BG Bau	Berufsgenossenschaft der Bauwirtschaft / German insurance association for the construction industry
CAS	Chemical Abstracts Service
CGS	control guidance sheets
CMR	carcinogenic, mutagenic, toxic to reproduction
CNT	carbon nanotubes
DGUV	Deutsche Gesetzliche Unfallversicherung / German Social Accident Insurance
DIN	Deutsches Institut für Normung e.V. / German Institute for Standardization
ECHA	European Chemicals Agency
EU-OSHA	European Agency for Safety and Health at Work
G/D	Gas/Dust
GHS	Globally Harmonised System
HSE	Health and Safety Executive
IFA	Institut für Arbeitsschutz der Deutschen Gesetzlichen Unfallversicherung / Institute for Occupational Safety and Health of the German Social Accident Insurance
LEV	local exhaust ventilation
MSDS	material safety data sheet
PAPR	power air-purifying respirator
PPE	personal protective equipment
REACH	registration, evaluation, authorisation and restriction of chemicals
SME	small and medium enterprises
STOP	Substitution, technical measures, organisational measures and personal protection measures
TRGS	Technische Regel für Gefahrstoffe / Technical Rule for Hazardous Substances
GefStoffV	German Hazardous Substances Ordinance
VdL	Verband der deutschen Lack- und Druckfarbenindustrie e.V. / German association of the coatings and printing ink industries
WHO	World Health Organisation

2 Summary

A rising number of companies, especially small and medium enterprises (SME), are active in the field of nanotechnology. For safe development of this industry, forethought of occupational safety and health considerations is important. This guideline on good working practice with nanomaterials addresses research institutions as well as SME industries. **Four decision criteria** are presented that support the reader in deriving the appropriate occupational safety measures in a comprehensible way. These occupational safety measures are tailored to the defined groups of nanomaterials and follow the precautionary approach. They comply with the priority list of the STOP principle: substitution, technical measures, organisational measures and personal protection measures.

❖ **Four decision criteria can be implemented in risk assessment to find appropriate risk reduction strategies.**



3 Introduction

Nanotechnology is a widely applied cross-sectional technology with innovations in almost all industry sectors. Beyond the 300,000 to 400,000 jobs directly involved in nanotechnology in Europe, an even larger number of workplaces down the supply chain are involved in using manufactured nanomaterials (EU-OSHA 2012). Hence, a huge number of companies, especially small and medium enterprises (SME), handle nanomaterials. For this reason, it is a challenge to provide support for a sustainable development compatible to both human health and the environment, and to simultaneously exploit this prosperous industry to its greatest potential. This guideline presents **decision criteria for general safety strategies** expanded with suggestions of **specific protection measures** for the defined groups of nanomaterials. It is based on a document with the intention to provide guidance for partner laboratories, which were synthesizing, testing and measuring nanomaterials in order to develop reference methods and materials.

Within the EU FP7 NanoValid project, risk reduction strategies for occupational handling were developed based on a variety of tested and validated methods and materials. This guideline was written to provide recommendations for good occupational health and safety measures that are following a precautionary approach.

❖ **A huge number of new substances on the market can be handled according to a precautionary approach. This is also applicable to newly generated nanomaterials.**

Protection measures for handling nanomaterials are derived based on our general knowledge about occupational safety and health at workplaces, where chemicals are handled. Chemical hazards are generally affecting safety and health of workers at workplaces, whereby only a small minority of the approximately 100,000 substances on the market are classified in a system for their hazardous properties. Moreover, within this minority, a complete data set on hazardous properties exists only for a small number of substances. If unknown substances are handled, certain hazardous properties are assumed using a **precautionary approach**.

❖ **Substances with known hazardous properties can be handled with well-founded risk reduction strategies. This approach can be adopted for nanomaterials if one knows the workplace situation and the category of the nanomaterial.**

This precautionary approach applies until these hazardous properties can be rebutted. During the history of occupational safety assessment, levels of protection measures used have evolved. These are adapted for the different hazardous properties and different exposure levels – and also for a situation of unknown, or incomplete, hazard data. From this well-founded pool of chemical risk assessment, one can derive **measures specifically tailored** for workplace situations concerning specific types or categories of nanomaterials.



❖ **Control guidance sheets (CGS) for typical work processes can be used additionally. They are provided by several institutions, for instance by HSE or BAuA.**

The present guide on safe handling of nanomaterials has been generated by considering a number of existing safety guidelines. However, there is a vast number of distinct activities and publications regarding safe handling of nanomaterials; and moreover, a wealth of legal obligations, which are defined for handling hazardous chemicals at workplaces and protections of workers from chemical risks (for instance the German Hazardous Substances Ordinance (GefStoffV)). These publications cannot be explained in greater depths at this point. These legal requirements are in compliance with the demands from corresponding EU directives. However, the respective national legislations of the member states have to be considered in addition. **For several typical recurring work processes in everyday situations, such as powder weighing, control guidance sheets (CGS) can be used in addition, to facilitate the risk assessment.** They are provided by several institutions, for instance the Health and Safety Executive (HSE: www.hse.gov.uk/pubns/guidance/) in the United Kingdom or the Federal Institute of Occupational Safety and Health (BAuA: www.baua.de/en/Topics-from-A-to-Z/Hazardous-Substances/EMKG/Control-guidance-sheets.html) in Germany. The control guidance sheets offer practical advice on how to avoid or reduce the risk to workers.



4 Routes of exposure

All chemical substances can pose health and safety risks via potential inhalative, dermal or oral uptake, which also applies to nanomaterials. **In occupational settings, inhalation and dermal exposure is given priority.**

The protection measures listed here apply:

1. mainly to dry, dusty nanoparticles or -fibres and their agglomerates and aggregates
2. to nanoparticles dissolved in liquid formulation
3. to nanomaterials bound in solid matrix

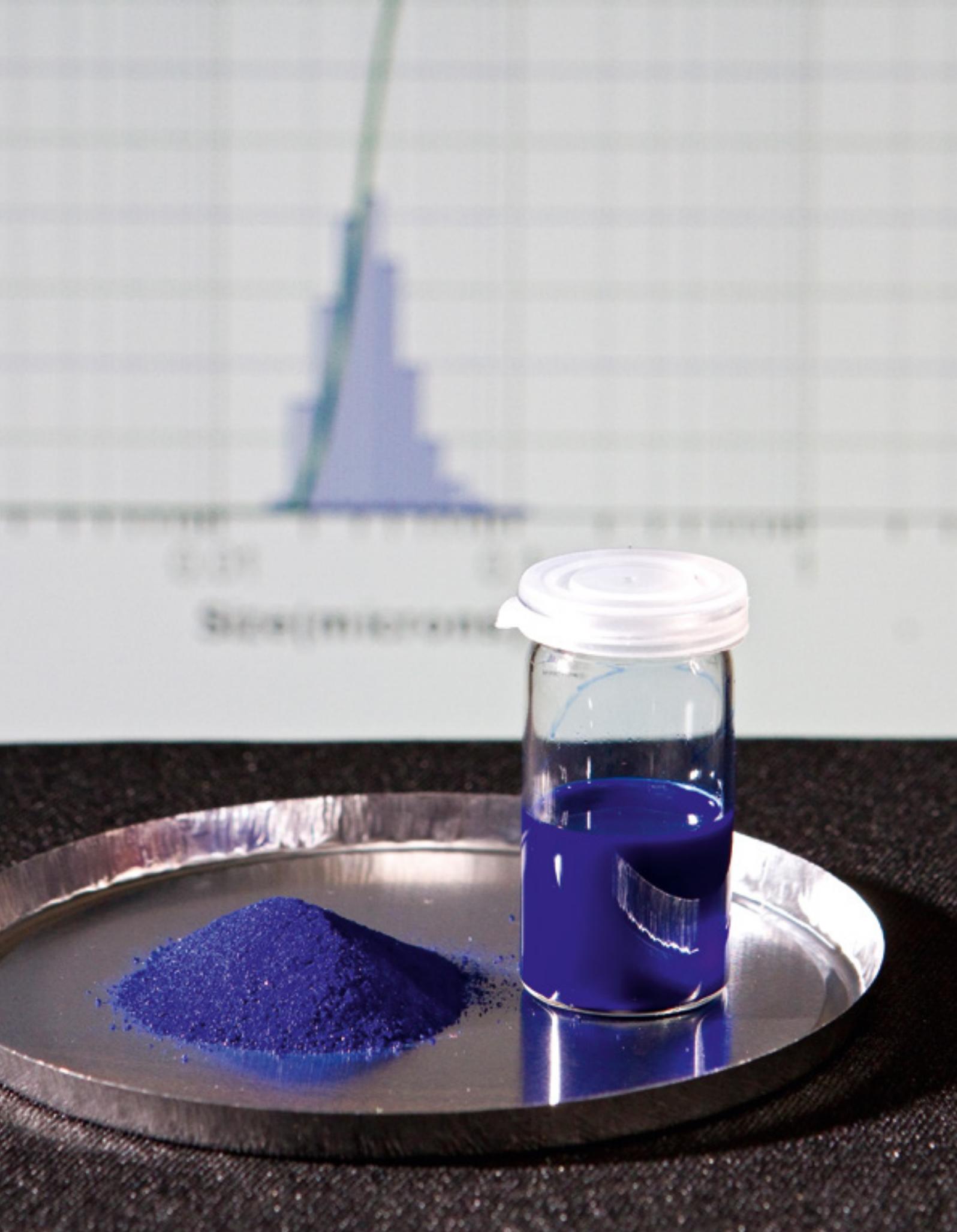
Potential routes of exposure are classified in the following list:

1. Inhalation—The most common route of exposure is by inhalation. The uptake of airborne nanoparticles into the respiratory system may also occur during processing and packaging of dry powder, during nanomaterial synthesis or during spraying processes.
2. Dermal—Dermal exposure to nanomaterials has received much attention, perhaps due to concerns regarding both occupational exposure and the introduction of nanomaterials in cosmetics. Dermal exposure may also occur during set up, cleaning and maintenance.
3. Oral—Workers can be exposed by unintentional hand-to-mouth transfer of materials or swallowed particles may get deposited on mucosae of the gastrointestinal tract and can occur following mucociliary removal of materials from the respiratory tract. In occupational safety, the risk of oral uptake is significantly reduced by general hygiene measures.

Factors affecting exposure to nanoparticles include:

1. the amount of material being used;
2. the susceptibility of material to be easily dispersed (in the case of a powder) or to form airborne sprays or aerosols (in the case of suspensions);
3. the degree of containment and duration of use.

To increase occupational safety, collective and personal protective equipment should be evaluated and improved for reducing workplace exposures to nanoparticles.



5 Decision criteria to derive occupational safety

The hazard level is determined based on a risk assessment. This depends a) on the hazardous properties of the nanomaterial and b) on the exposure level. From risk assessment, occupational safety measures can be derived following the priority list of the STOP principle: **S**ubstitution, **T**echnical measures, **O**rganisational measures and **P**ersonal protection measures (AGS 2008b, AGS 2010).

The appropriate occupational safety measures can be determined using evaluation criteria. The recommendations should be adapted to the respective national legislation of the respective member state.

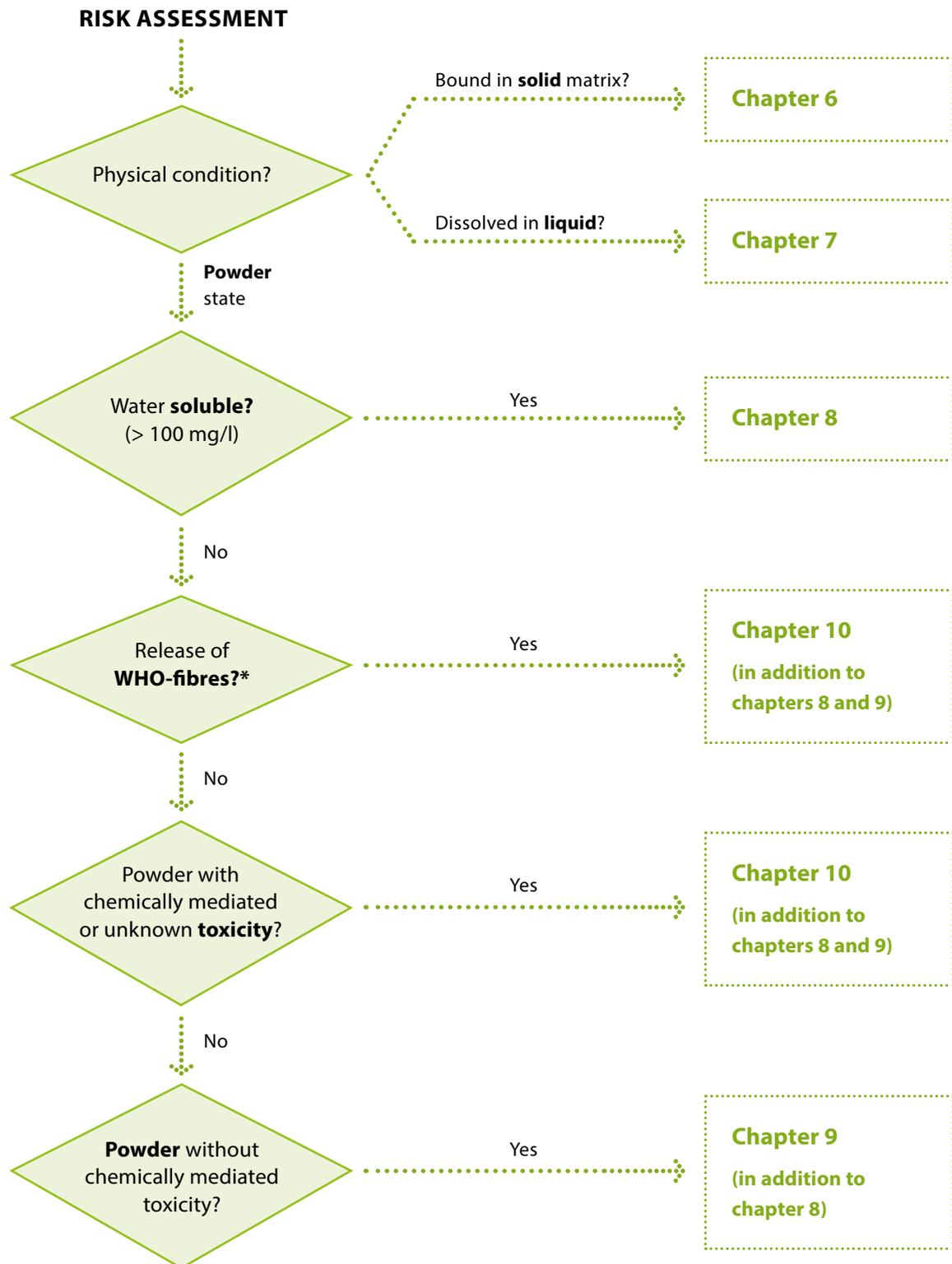
The decision criteria evaluate:

1. the **physical condition** of the nanomaterial:
 - a. if it is fixed to a **matrix**
 - b. if it is suspended in a **liquid**
 - c. if it occurs as dry **powder**
2. if the nanomaterial is well **soluble** in water
3. if the nanomaterial is a **fibre** according to WHO criteria or if it has been determined that the nanomaterial is carcinogenic, mutagenic or toxic to reproduction (**CMR**)
4. If the powder has a **chemically mediated toxicity** or exhibits **only particle toxicology** of the substance itself (therefore an **inert dust with solely particle toxicology**)

❖ The decision criteria can support the risk assessment of activities with nanomaterials and lead to an appropriate safety strategy.

A flow chart (Figure 1) was prepared to determine the correct criteria to follow in order to identify appropriate occupational safety measures.

The presented occupational safety measures are influenced by the quantity, the release potential, as well as the exposure level of the respective nanomaterial. A wide range of guidelines published from different institutions can additionally provide support in deriving the appropriate occupational safety measures. They refer either specifically to handling nanomaterials or more generally to handling chemicals of the respective hazard groups and can additionally provide support in deriving the appropriate occupational safety measures.



* for definition of WHO-fibres see chapter 5.3

FIGURE 1: FLOW CHART ON CRITERIA FOR CHOOSING THE APPROPRIATE PROTECTION MEASURE LEVEL

5.1 Decision criterion 1: Physical condition of the nanomaterial

The **first decision criterion** considers the physical condition of the nanomaterial. Since inhalation is a major route of exposure in occupational safety, the potential exposure due to the generation of dusts or aerosols is given priority.

At first, it has to be clarified if dusts or aerosols can occur during a specific activity with the nanomaterial. Hence, the initial question is if the nanomaterial is fixed in a **matrix**, if it is suspended in a **liquid** or if it occurs as dry **powder**.

5.1.1 Nanomaterials fixed in matrix

The German association of the coatings and printing ink industries (VdL) has commissioned studies about the potential release of nanoparticles from coating matrices (VdL 2012). First investigations revealed that the added nanoparticles themselves are not released in everyday use (VdL 2012). The nanoparticles stay bound within the abraded particles even if the surface is sanded or weathered (VdL 2012). From these insights one can conclude that an individual risk assessment, which refers to the respective activity like grinding or milling, is suitable for handling nanomaterials bound in a matrix. A number of recommendations for activities with nanomaterials fixed in a matrix are given in **chapter 6**.

❖ **Chapter 6 provides recommendations for nanomaterials fixed in matrix.**

5.1.2 Nanomaterials suspended in liquids

If nanomaterials are suspended in liquid formulations, one should avoid activities like spraying, where aerosols can occur. If the occurrence of aerosols can be excluded, an individual risk assessment of the workplace considering standardised working methods is sufficient. However, if aerosols appear, it is necessary to derive occupational safety measures for aerosol applications. In **chapter 7** recommendations for handling nanomaterials in aerosol applications are given.

❖ **Chapter 7 provides recommendations for nanomaterials suspended in liquids.**

5.1.3 Nanomaterials in powder state

If nanomaterials are handled in powder form, decision **criterion 2** provides further support in deriving the right occupational safety measures.

5.2 Decision criterion 2: Solubility of the nanomaterial

Sufficient water solubility is the **second decision criterion**, since water soluble nanomaterials dissolve and then are present as molecules or ions, in other words they lose their “nanomaterial” properties and the assessment can be based on the traditional chemical toxicity. The primary issue for the hazardous effect of inhaled dust is the degradation time within the human body. A sufficiently soluble substance is degraded by the body within a reasonable time and is hence not biopersistent. This effect is dependent on the solubility of the substance. There is growing evidence that biopersistent dusts and fibres can result in inflammation and even cancer.

A water solubility value of more or less than 100 mg/l has been chosen as differentiator between the terms “sufficiently” and “sparingly” soluble substances used in this document. This differentiator is derived based on the example of amorphous silicon dioxide (CAS No: 7631-86-9) with a water solubility value of 120 mg/l.

Insoluble or sparingly soluble dusts, which are also named “granular biopersistent dusts”, have a water solubility of less than 100 mg/l. However, amorphous silicon dioxide does not show the typical effects of insoluble or sparingly soluble dusts which can be explained due to its solubility value of 120 mg/l. For this reason, the differentiator point of 100 mg/l seems plausible.

Good water solubility normally also hints to a good solubility in biological media, and vice versa. However, in individual cases a sparingly water soluble substance like cobalt metal can in contrast be well soluble in serum. For this reason, the particular exceptional case of potential good serum solubility despite sparingly water solubility can be examined by a case by case analysis.

5.2.1 Sufficiently soluble nanomaterials

If the nanomaterial shows water solubility **higher than 100 mg/l**, it is termed in this context as sufficiently water soluble. In this case, it is sufficient to derive measures for dust reduction considering the classification of the respective microscale substance. **Chapter 8** shows several occupational safety measures for dust reduction.

❖ **Chapter 8 provides recommendations for sufficiently soluble nanomaterials in powder form. The toxicology of the microscale form of the substance has to be regarded additionally.**

5.2.2 Sparingly soluble nanomaterials

The majority of the synthesized nanomaterials are sparingly soluble with a solubility value **lower than 100 mg/l**. In this case, decision **criterion 3** provides support in deriving the right occupational safety measures.

5.3 Decision criterion 3: Fibre morphology

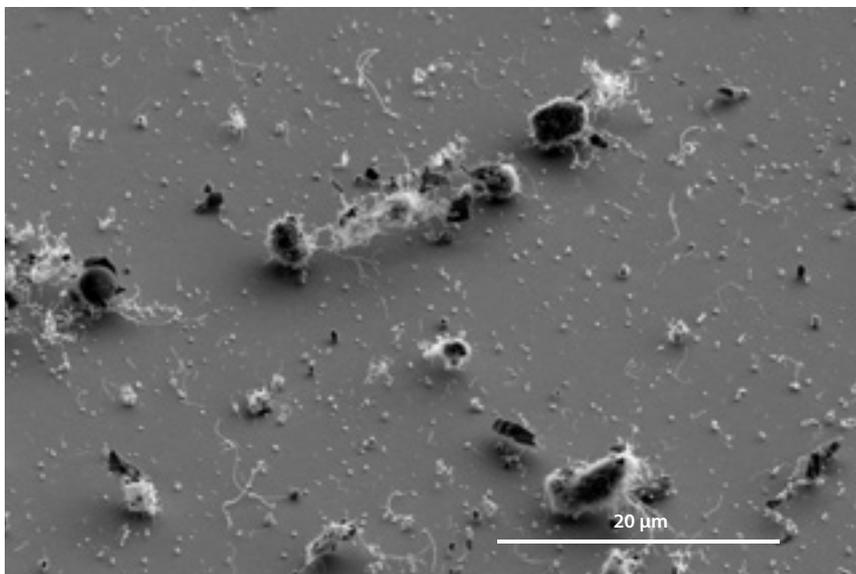
The **criterion 3** on fibre morphology can markedly step up the assumed hazardous properties. Therefore it should additionally be checked if this criterion applies in any case.

The microscale and the nanoscale form of a chemical substance can differ both morphologically and toxicologically. This also applies for fibres, whereby nanoscale fibres are not only different from the respective microscaled (“bulk”) substance, but there are also differences between the various fibre types. Flexible fibres can stick together and form a structure resembling a ball of wool; whereas stiff fibres are fragile and can break. Certain carbon nanotubes with a needle-like fibre shape have been compared to asbestos showing the same asbestos-like, length-dependent and pathogenic behaviour in the mouse model [Poland et al., 2008]. For this reason, a differentiated precautionary view of fibre types is required.

A relevant dimension for fibre-specific toxicity is the WHO (world health organisation) fibre principle (**WHO criteria**): WHO fibres are characterised by a **length of > 5 µm**, a **diameter of < 3 µm**, and an **aspect ratio (length-to-diameter) of > 3 : 1**.

Fibres that do not meet these criteria can be generally regarded as non-carcinogenic, but if **WHO criteria apply** or if a morphological examination does not exist, for precautionary reasons the fibres should be **treated as carcinogenic** substances (Carc. 1). If the toxicology of fibres regarding carcinogenicity is examined, the detection method given in the regulation No 1272/2008 on classification, labelling and packaging of substances and mixtures, annex VI, point 1.1.3.1, note Q and R (GHS 2008) should be followed instead of using the AMES test. The AMES test is not regarded as meaningful in case of detecting carcinogenicity due to a morphological structure, i. e. fibres are not recognized by this test.

If the MSDS does not clarify the question of whether the WHO criteria are applicable and if the fibres are rigid and friable or flexible, we recommend to contact the manufacturer for instance with the “sample letter for questions” (**chapter 14**).



Scanning electron microscope (SEM) picture of carbon nanotube agglomerates and single fibres.

❖ **Chapter 10 provides recommendations for nanofibres, which are rigid and meet the WHO criteria. If the nanofibres are flexible, do not break or do not meet the WHO criteria, chapter 9 can give information on safe handling.**

5.4 Decision criterion 4: Toxicity of the substance (particle toxicity and chemically mediated toxicity)

If nanomaterials are not soluble, contain/release no WHO fibres, and are present in a powder state, two more options have to be considered:

- a.) The substance has **no chemically mediated toxicity**, but exhibits **toxicity due to particle morphology** or powder state.

Particle toxicity refers to a potential for the release of granular, biopersistent and respirable particles (GBR), which can cause harm upon accumulation over time (if the substance is not soluble – see decision criterion 2). For this respirable dust, a safety strategy can be generated using the measures recommended in **chapter 9**. It should be attempted to maintain an exposure level of 0.5 mg/m³ (AGS 2013).

❖ **Chapter 9 provides recommendations for sparingly soluble nanomaterials in powder form, which have no chemically mediated toxicity, but exhibit typical particle toxicity due to their morphology.**

However, it is also possible that

- b.) the substance possesses a “substance-specific”, **chemically mediated toxicity** and is hence classified as hazardous. Usually, a chemically mediated toxicity refers to the microscaled form and – if unknown and not stated otherwise - can be assumed for the nanoscaled form, too.

Chemically mediated toxicity is caused e.g. by the release of toxicants (e.g. ions), by chemically functional groups, or by catalytic activity. Specific occupational exposure limit values exist for a number of (microscaled) substances with specific toxic properties. These values are typically lower than 0.1 mg/m³. If this value is not exceeded, for instance with a material of low dustiness or if small amounts are used, then the recommendations in **chapter 9** are sufficient. If the value is exceeded, the strategy shown in **chapter 9** should be superseded by the safety strategy in **chapter 10**. A safety strategy for nanoscaled substances with specific toxic properties should be based on the classification of the respective microscaled material, if no concrete deviating classification of the nanoscaled form is present (AGS 2013).

❖ **If the powder has a known chemically mediated toxicity, chapter 10 can be consulted. An exception can be made in case of a material with low dustiness or if small amounts are used.**

5.5 Handling nanomaterials in laboratories

Activities with chemicals under laboratory conditions can result in specific recommendations in the respective chapters in case the safety strategies differ. Although **smaller quantities** of chemical substances are used, particle handling is often **performed more frequently** during repeated short-time activities outside a closed system. Furthermore, the safety strategy in laboratories is influenced by the specific building specifications and the high qualification of the laboratory personnel. Therefore, the recommendations on handling nanomaterials under laboratory conditions should comply with the construction, the equipment and the operation of the laboratory as well as with the qualification of the workers (DGUV 2008). For laboratories, it is generally recommended to handle new or not sufficiently studied substances only in a fume hood or in equipment at a comparably high safety level (DGUV 2008, AGS 2008a). Furthermore, it is suggested to handle new substances, where the properties of toxicity, irritation, carcinogenicity and skin sensitization, as well as physico-chemical properties are insufficiently known, with greater caution (DGUV 2008, AGS 2008a, AGS 2010). Comprehensive recommendations on safe handling in laboratories can be found for instance in the book "Working Safely in Laboratories" (DGUV 2008) or in the TRGS 526 (AGS 2008a).



Handling substances in a fume hood

5.6 Specific information in the material safety data sheet

In order to correctly assess the hazardous properties of the nanoscale substance, information provided in the form of a material safety data sheet (MSDS) is always required. Here, it should be ensured that the information about the toxicological and physicochemical properties within the MSDS specifically refers to the respective nanomaterial.

A professional user will usually get a MSDS from the manufacturer or importer. A MSDS always has to be provided for substances which are classified as hazardous. In addition, MSDS will often be provided for non-hazardous substances in order to inform the user about certain properties of the substance.

The information in the MSDS should explicitly include the nanoscale form, i.e. it should contain information regarding the hazardous properties of the nanoscale form, since the microscaled and the nanoscale form of the same chemical substance can be morphologically and toxicologically different.

For this reason, it should be noted in the MSDS if the following test data on the hazardous properties refer to the respective nanoscale form of the substance:

1. acute toxicity (Acute Tox. 3)
2. irritation (Skin Irrit. 2)
3. skin sensitization (Skin Sens. 1)
4. mutagenicity (Muta. 2)

The nanoscale form can be described in the MSDS further by information about particle size and specific surface.

If fibres are handled, the morphological information of the WHO criteria is relevant. The WHO criteria apply if the fibre is longer than 5 µm and if the aspect ratio is higher than 1 :3. A fibre according to WHO should be treated as carcinogenic for precautionary reasons (see chapter 5.3 "Decision criterion 3: Fibre morphology"). However, a fibre shorter than 5 µm with a length-diameter-ratio below 1 :3 can be regarded as nanoscale dust.

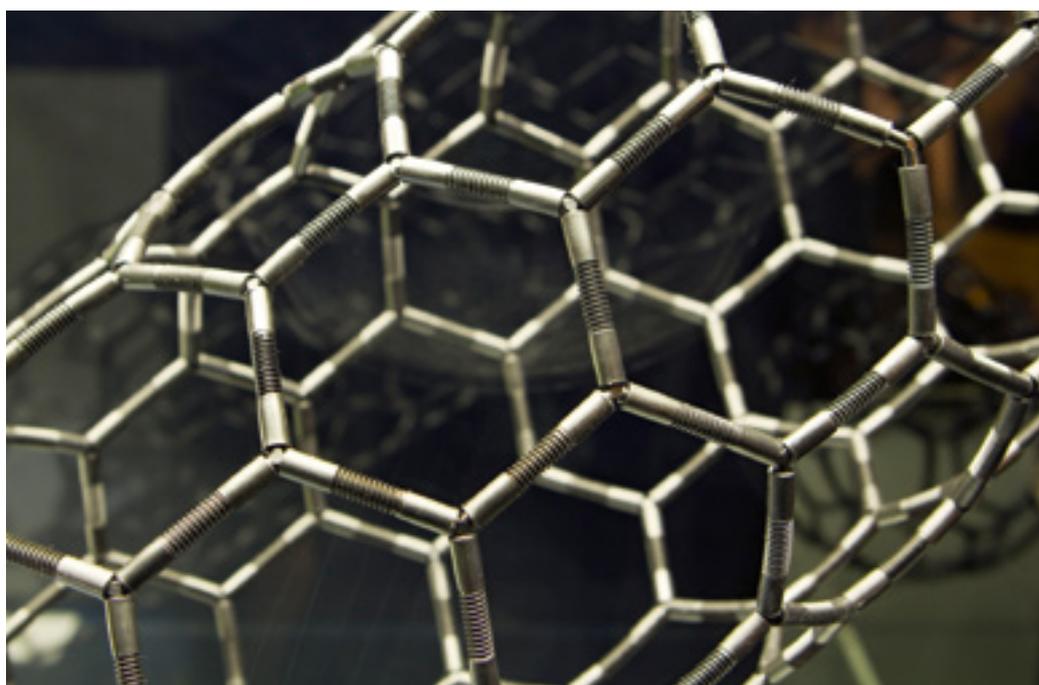
If the MSDS lacks the information about the specific hazardous properties of the nanomaterial, it is recommended to **ask the manufacturer**. **Chapter 14** contains a sample letter for questions addressed to a manufacturer.

In cases when a) a substance is newly generated and information on the hazardous properties has not yet been determined or b) information on the hazardous properties are missing in an existing MSDS, the following hazardous properties should be assumed:

HAZARDOUS PROPERTY	RISK PHRASE	HAZARD STATEMENT
Acute toxicity (Acute Tox. 3)	R23, R24, R25	H301, H311, H331
Irritation (Skin Irrit. 2)	R38	H315
Mutagenicity (Muta. 2)	R68	H341
Skin sensitization (Skin Sens. 1)	R43	H317

TABLE 1: CORRELATION OF HAZARDOUS PROPERTIES AND RISK/HAZARD STATEMENTS

Newly synthesized nanomaterials belong to the group of insufficiently examined substances. Therefore, this approach is applicable not only for new substances but also for newly synthesised nanomaterials. However, if a legal classification is known and nanomaterials are handled for longer periods, the protection measures can be based on this classification – this may for instance apply to many partly-nanoscale pigments.



Model of a carbon nanotube



6 Protection measures for handling of nanoparticles bound in a matrix

The recommendations in this chapter are partly cited from the German insurance association for the construction industry (BG Bau 2012).

6.1 Substitution

- Use of low-dust materials is preferred (e. g. humidified raw material, granules, pastes).
- Low-dust processing methods reduce the dust load (for instance wet or damp processing techniques).

6.2 Technical protection measures

- Nanoproducts generated mechanically, e.g. by grinding or milling, should only be removed using exhausted vacuum cleaners/dust collectors with a dust grade M or higher.
- Equipment such as exhaust hoods or local exhaust ventilation (LEV) should be examined and tested against its performance standard – typically once a year.
- The exhaust air must only be routed back to the working area after sufficient cleaning using approved equipment.

6.3 Occupational safety measures

- Directly collect the contents of the vacuum cleaner for disposal.
- Check the function and extraction performance of the vacuum cleaner during the activity. Directly remove suction hose blockages.
- The equipment should be checked regularly and maintained at least annually.

6.4 Effectiveness check

- The effectiveness of the safety strategy can be assessed either with or without technical measures.
- Exposure measurement with technical measures: For dust concentrations, threshold values are available. One example is the value of respirable dust (with a density of 2.5 g/cm^3) of 1.25 mg/m^3 (AGS 2014) determined by the German Committee on Hazardous Substances (AGS). It is recommended to consider the respective national legislation.
- Exposure assessment without technical measures: either consider workplaces with comparable hazard and exposure situation or use calculation methods.



Visual control of a coated surface

7 Protection measures for handling of nanoparticles dissolved in liquids

The recommendations in this chapter are partly cited from the HSE control guidance sheets (COSHH essentials 220, 221, 319, 322), the BAuA control guidance sheet drafts for biocides, and the German BG rule 231 from the Federation of Institutions for Statutory Accident Insurance and Prevention (HVBG 2006).

Several exposure situations exist for handling liquids. There are low aerosol processes like painting or dipping, and processes which may be considered high aerosol processes such as spraying. With respect to varnishing, spraying can be 1) isolated in a spray cabinet, 2) carried out at an extraction wall or 3), for smaller quantities, be performed in front of a spray wall.

A **spray cabinet** is a closed room with technical ventilation (supply air, extracted air, velocity of the air flow 0.3 m/s), which guides the air vertically, horizontally or as a combination of both. During spraying, the sprayer and the object to be sprayed are inside this closed room.

At an **extraction wall**, the object is positioned at a spraystand inside an area, which is closed except for the open entry side. The sprayer is located next to the open entry side, from where the air is supplied. The object is positioned between the extraction wall and the sprayer. The spray jet is directed towards the extraction wall (deviation $< 30^\circ$ from central axis).

A **spray wall** is positioned next to the object during spraying in order to capture surplus aerosols. The position of the sprayer and the direction of the spray jet are not defined. The capture effectiveness is relatively low.

7.1 Substitution

- Avoid methods with exposure to aerosols. Since aerosols can occur during spraying, alternative methods are preferred such as dipping, coating or rolling processes. Automated processes are an exception since they do not require the presence of a worker.

7.2 Technical protection measures

- If you cannot avoid spraying, consider the proposed measures in **chapter 9.5** “Explosion protection”. However, since hybrid mixtures of dusts and liquids are generally regarded as more hazardous than dusts alone, the equipment should also be in compliance with the equipment category 1 G/D (Directive 1994).
- An automated application is preferred over a manual application.
- Good exhaust air ventilation is considered a necessity.
- If the spray application is performed at an extraction or spray wall, the atomized spray should be captured locally as close as possible to the source.

7.3 Organisational protection measures

- The inhalation of spray or aerosols is to be avoided. If the spraying is performed outdoors, the wind direction should be determined before starting, with the activity performed directionally with the wind flow.
- After spraying, the exposure decreases slowly. Therefore, a spray cabinet shall be entered only after particles have settled.
- It should be noted within the written instructions that a potential hazardous substances may occur in nanoscale.
- The recommendations regarding protection measures, explosion protection and waste removal should also be included in the operating instructions.
- In the case where pollution is visible, the personal protective equipment needs to be exchanged after the spray application. Visibly polluted skin needs to be washed.

7.4 Personal protection measures

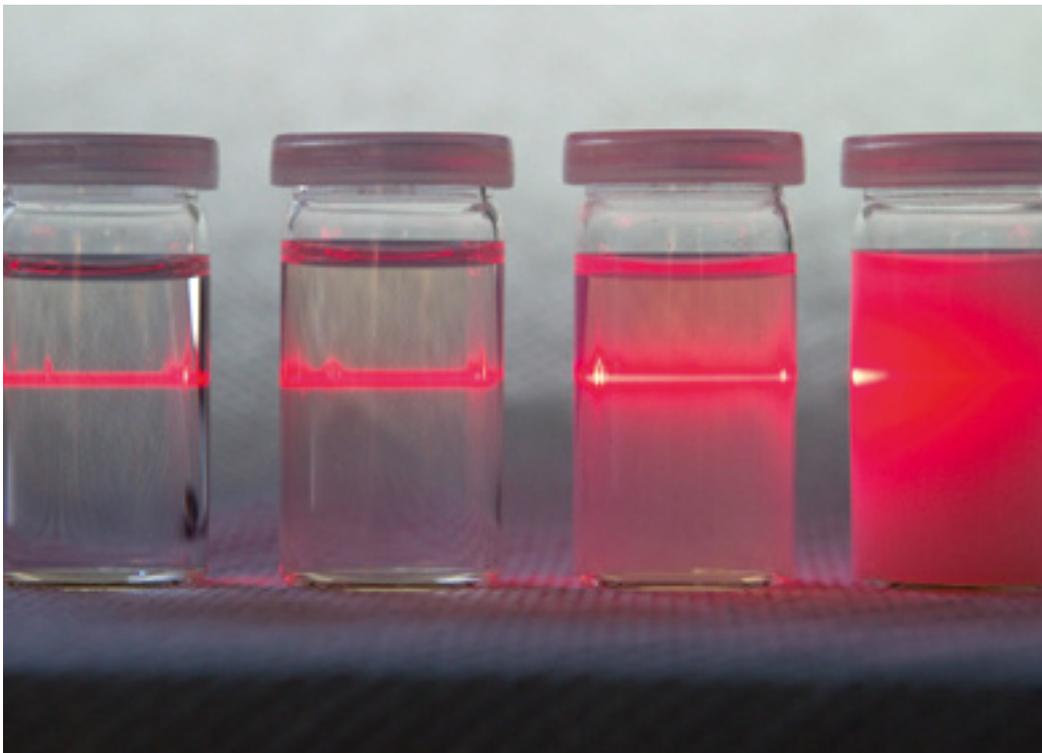
If technical and organisational measures are not sufficient or cannot be applied, personal protection equipment (PPE) is required:

- If a closed spray cabinet is entered, PPE should be worn. However, PPE requirements are activity-related when considering an extraction or spray wall.
- Respiratory protection: if aerosols are generated, it is recommended to wear a mask with a combination filter such as a 2-P2, which is applicable for vapours and particles. Furthermore, it is recommended to consult the MSDS for choice of mask, to provide the appropriate level of protection for the level of exposure.

- Hand protection: regarding nanomaterials in liquids, chemical resistant gloves made from materials such as nitrile or neoprene provide an adequate level of protection. In this respect, the permeation time and the chemical compatibility of the glove material with the respective nanomaterial and liquid should be taken into account. Contaminated gloves should be changed immediately.
- The protective suit needs to be chosen with regards to the specific exposure situation. In the case of a spraying application, a protective suit type 4 should be worn.
- The PPE is provided and cleaned by the employer. It is present in sufficient quantities and in necessary sizes.

7.5 Effectiveness check

- The effectiveness of the safety strategy can be assessed either with or without technical measures.
- Exposure assessment with a non-measurement method: either consider workplaces with comparable hazard and exposure situation or use calculation methods.



Tyndall effect of nanoparticles in solution



8 General protection measures for handling of soluble powders

The recommendations in this chapter are partly cited from the control guidance sheets provided by the Federal Institute for Occupational Safety and Health (BAuA 2012) and from the Announcement on Hazardous Substances 527 (AGS 2013). The safety strategy can be derived according to this chapter. Additionally, the legal classification of microscaled substances needs to be considered.

8.1 Substitution

- Use of low-dust materials is preferred (e. g. humidified raw material, granules, pastes, readymixed material such as mortar or putty).
- Low-dust processing methods reduce the dust load (e. g. dust-proof equipment, wet or damp processing techniques, or wetting of cargoes and bulk materials).

8.2 Technical protection measures

- Provide a suitable LEV at the release or discharge point to collect dusts and dispose of them safely.
- The exhaust air must only be carried back to the working area after sufficient cleaning using approved equipment.
- Ensure that air flows past the worker and then past the work activity to the extraction point.
- In the case of hand-held machines (e. g. cut-off grinders, slot and plaster milling machines or grinding devices), only use tested systems with extraction. Several providers offer suitable equipment with dust collecting elements and dust removers.
- Before entry into service, check the efficiency of the appliances for dust separation, collection and deposition.
- As a minimum, the occupational exposure limit values for the inhalable (10 mg/m^3) and the alveolar (1.25 mg/m^3) dust fraction must be respected (AGS 2014).

- Check, maintain and service all equipment regularly, at least once a year, e.g. filter and extraction performance.
- Maintain and service all facilities and equipment as advised by the manufacturer.

8.3 Organisational protection measures

- Prevent the spread of dust into uncontaminated work areas, for instance by sticky mats at the entrance, which should be exchanged weekly.
- Drop heights of discharge, filling and dumping points should be minimised and dust-proof casings should be incorporated where possible.
- Avoid surfaces on which dust can be deposited, e.g. textile surfaces and hard-to-reach coverings.
- The LEV should be switched on and be working before the workers start dust processing methods.
- If possible, the emptied sacks should be folded, bundled and pressed in a dust extraction system.
- When cleaning up and disposing of spilled solids, do not disturb dust unnecessarily. Wet-clean or vacuum dusts. Use approved industrial vacuum cleaners with dust category "H", according to the standard DIN EN 60335-2-69, for removal.
- Do not clean up with a dry brush or compressed air.
- If nanomaterials are cleaned by wet processes, a strong water jet should be avoided in order to avoid friction and raising dusts.
- All surfaces, which come into contact with powders, should be dry before commencement of the activity, in order to avoid dust deposits.
- Ensure that bags and other waste are not drawn into the ventilation duct.
- Dispose dust deposits in the work and storage areas regularly in order to reduce risk of fire.
- Review that these basic measures and proper disposal are complied with during regular site inspections.
- Washrooms should be available in case of short-term high dust loads and non-compliance with occupational exposure limits.
- It should be assessed, and – where required – put into practice, if medical consultations need to be arranged or offered (see **chapter 11.2-3**).
- Dust generating agents must be preserved and stored in closed containers, silos, bunkers, shipping containers, or in dust-proof bags.

- Cover bulk goods and open containers.
- Workers should do outdoor work with their backs toward the wind and avoid standing in the dust plume.

8.4 Personal protection measures

Personal protection measures (PPE) are required in case of short-term high dust loads and non-compliance with occupational exposure limits:

- Respirator (with P2 particle filter), protective clothing and goggles should be worn. The use of the respirator mask should be restricted, according to the type of mask.
- If the activity is over a long period of time, then power air purifying respirators (PAPR) with particle filter TM2P are recommended from an ergonomically point of view. The PAPR avoids inhalation air resistance since the air flows is battery-driven through a hand-held filter prior to worker respiration.
- Use, maintain and store any PPE provided in accordance with instructions.
- The PPE should be provided and cleaned by the employer – and should be available in sufficient quantities and in necessary sizes.
- Wear suitable work clothes and change contaminated work clothes immediately.
- Off-site clothing should be stored separately from work clothing.
- Do not shake work clothing or subject to compressed air.

8.5 Effectiveness check

- The effectiveness of the safety strategy can be assessed either with or without technical measures.
- Exposure assessment with a non-measurement method: either consider workplaces with comparable hazard and exposure situation or use calculation methods.



Local exhaust ventilation



9 Protection measures for dry, dusty and insoluble nanomaterials

The recommendations in this chapter are partly cited from the Announcement on Hazardous Substances 527 (AGS 2013), from a recommendation guideline published by BAuA and VCI (BAuA-VCI 2012) and from the control guidance sheets (BAuA 2012). These recommendations **supplement** the recommendations of **chapter 8** "Solubility of the nanomaterial: General protection measures for handling soluble powders".

9.1 Substitution

- Substitution shall be performed if technically and economically feasible.
- Consider whether hazardous substances or processes can be substituted by less hazardous ones (for instance substances with reduced emissions).
- Lower hazardous properties: the hazard potential can, where applicable, be reduced by a modification of the surface for instance via coating.
- Lower dust release: dry, dusty nanoparticles can be dispersed in liquid media, bonded in permanent matrices or replaced by materials generating less dust (through moistening, granulates, pastes or premixed materials). The dust release can also be reduced by moistening the nanopowder. We recommend asking the manufacturer about the dustiness of the nanopowder.

9.2 Technical protection measures

- Handling nanomaterials should be performed in a closed system, for instance a glove box. If gram quantities are used (i. e. in **laboratories**), fume exhaust hoods, safety cabinets or similar state-of-the-art equipment are regarded as emission free.
- Existing installations, which are not enclosed, should be retrofitted with suitable technical protective measures, when technically feasible. These are laboratory hoods, for example, as well as safety workbenches, glove boxes, extraction cabinets, object extraction systems or similar, state-of-the-art installations.
- If activities outside a closed system cannot be avoided, for instance during refilling or filling, dusts should be extracted at the source where possible.

- Equipment such as dust extractors for air recirculation should extract the air with a filtration rate of more than 99.995 %, for instance over a dust class “H” filter.
- Cleaning should be performed either by wet wiping or by vacuum cleaning with a dust class “H” filter according to DIN EN 60335-2-69.

9.3 Organisational protection measures

- It is necessary to inform the workers about particular physico-chemical and toxicological properties of handled nanomaterials and the respective required protection measures.
- If the nanomaterial is newly synthesized and certain hazardous properties (acute toxic (Acute Tox. 3), irritant (Skin Irrit. 2), skin sensitising (Skin Sens. 1), or mutagenic (Muta. 2)) are partially unknown, it should be highlighted that the handled substance is nanoscale, respectively that it still has unknown properties. For this reason it is recommended to e. g. add the phrase “Attention – substance not yet tested completely” additionally to the label of the already known properties from classification.
- Avoid dust deposits. If this is not feasible, remove dust deposits or spilled substances immediately by wet cleaning or by using suitable vacuum cleaners. It is not allowed to clean the working area by sweeping without dust binding measures or by blowing with compressed air.
- In the case of an unintentional release, for example a spillage of a larger amount of a dustgenerating nanomaterial (kg range):
 1. unprotected persons must leave or be evacuated from the work area, if necessary initiate emergency measures and inform workers in adjacent work areas,
 2. the work area may only be entered for cleaning work, when the dust cloud has settled. A dust-proof protective suit with a Type-5 certificate, chemical protection gloves and a tightly fitting respirator with a P3 filter should be worn in addition to work clothes consisting of trousers, jacket, safety shoes and eye protection,
 3. the contaminated work area should be cleaned with liquids and should only be re-opened for further use following a test for potential contamination,
 4. the spilled nanomaterial, the cleaning agents used and the contaminated protective clothing should be collected in tightly closing containers and be properly disposed of.

9.4 Personal protection measures

During short-term activities, the listed personal protection measures can be applied. Examples for these activities are filling processes, sampling as well as cleaning, maintenance and repair.

- Hand protection: chemical protective gloves made of materials such as nitrile or neoprene provide sufficient protection against nanomaterials in powdered state. In this respect, the permeation time and the chemical compatibility of the glove material with the respective nanomaterial should be taken into account.
- Respiratory protection: the efficiency of a respirator mask depends upon, amongst other aspects, its tight fit. The filter type is selected according to the exposure level during the **short-time activity** (dustiness and amount of the powder). Therefore, for short-time activity half-face masks with a **P2 particle filter** are recommended if the amount of respirable dust **does not exceed** the respective occupational exposure limit. An example for an occupational exposure limit value is **1.25 mg/m³** for respirable inert dust determined by the German Committee for Hazardous Substances (AGS 2013, AGS 2014). If it is not known (for instance from measurements or from comparable workplaces) if the occupational exposure limit value can be adhered to, or if this limit is exceeded (for instance in a case of unintentional release), half-face masks with **P3 particle filter** are recommended (AGS 2013). The usage time of the respirator mask has to be restricted, taking into consideration the respective type of mask.
- If the activity lasts over a longer period of time, then power air purifying respirators (PAPR) with particle filter TM2P or TM3P are recommended from an ergonomically point of view. The PAPR avoids an inhalation air resistance since the air flow is battery-driven and is routed through a hand-held filter prior to worker respiration.

9.5 Explosion protection

Some nanoparticles can have a higher explosion potential than larger sized particles. This is due to their smaller particle size and their higher surface area. The powdered state of substances with a size of 500 µm and smaller can form explosive dust/air mixtures. If explosive properties are present or unknown, protection measures against explosion should be applied. Explosive properties should be considered as a preventive measure especially for those oxidable nanoscale substances which generate a high amount of dust.

- If the risk of explosion of the handled nanoscale powder is unknown, ignition sources (such as smoking, electrical power, vehicles and battery charging) should be avoided by choosing the area zone 20 under ATEX and the equipment category 1D as a matter of precaution.



Explosion of dust

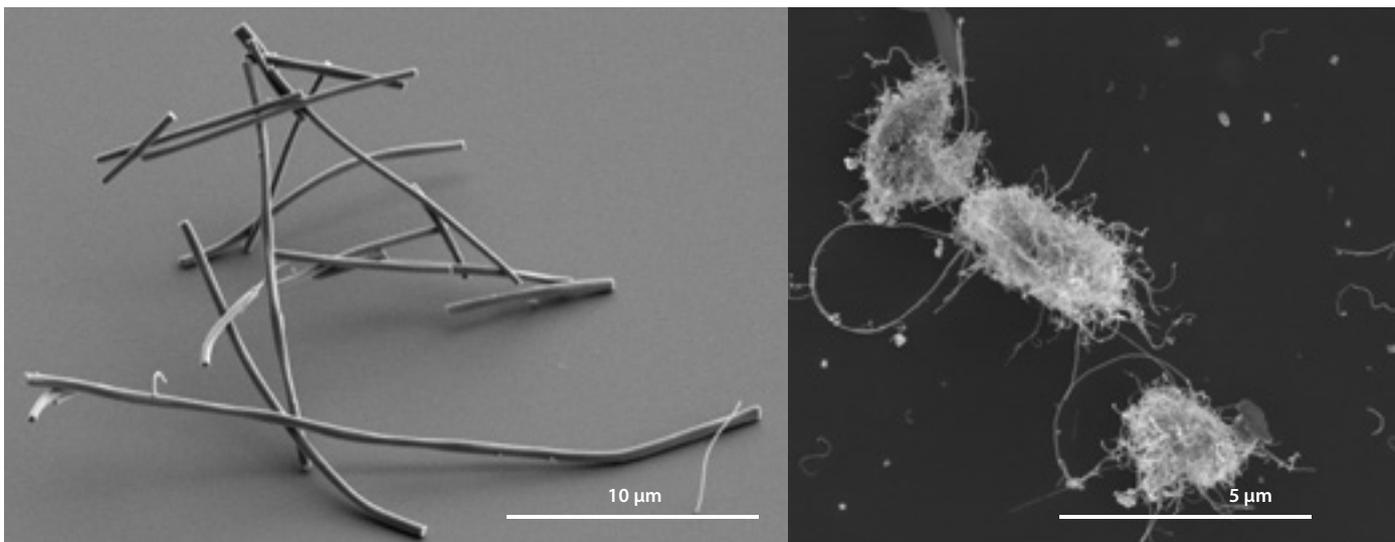
- Electrical systems, equipment (for instance the vacuum cleaner for removal of combustible dust) and transport devices should be ATEX certified (explosion protected) according to the EU-Directives 94/9/EC (Directive 1994) 1999/92/EC (Directive 1999) and follow the safety requirements of the respective field of activity.
- Static electricity shall be avoided by a providing a suitable grounding for the system, and utilisation of dissipative containers. For precautionary reasons, hot surfaces, flames and hot gases, as well as mechanically generated sparks, should not come into contact with nanoscale powders. The volume of containers made from insulating material is limited to a maximum of 5 liters.
- All insulating coatings of conductive containers are tightly connected to the container wall and not thicker than 2 mm.
- Within the area zone 20, it is prohibited to use battery powered devices (cordless screwdriver, hearing devices, mobile phones, radios, balances).
- Only authorised personnel, trained in the respective activities and specific handling procedures of explosion protection system and devices, are allowed to be present within the area zone 20.
- Within the area zone 20, the personnel should wear safety shoes with electrically conductive soles and should not change clothes, since there is a danger for electrostatic discharge.
- The area zone 20 should be labelled with a warning signage according to the specification of the ASR A1.3 (Explosive atmosphere hazard warning label).
- The periodic examination of the explosion protection system and the monitoring installation should be carried out by suitably competent persons or registered inspectors, for instance by an approved inspection agency.

9.6 Effectiveness check

- Exposure assessment with technical measures:
 - You can use screening measurements before and after implementing protection measures. Direct reading particle counting devices are very sensitive for the detection of leakages and of particles, which are not removed by an installed LEV.
 - It is recommended to use typical background concentrations of particles in urban environments as a reference level for improvement of current risk management measures and, if necessary, for further measurements to deepen the risk assessment: 20,000 particles/cm³ (particle density > 60,000 kg/m³) respectively 40,000 particles/cm³ (particle density < 60,000 kg/m³) (IFA 2012).

9.7 Placing on the market

- Nanomaterials should be transported as normal chemicals, i.e. in closed, labelled containers.
- Sending nanomaterials to the laboratories of other project partners is considered as placing on the market, which is defined within the Regulation (EC) No 1907/2006 of the European Parliament and of the Council of 18 December 2006 (REACH). According to REACH, placing on the market means supplying or making available to a third party, whether in return for payment or free of charge.
- According to article 31 of REACH, the supplier of a substance should provide the respective recipient with a MSDS compiled in accordance with Annex II of REACH, stating e.g. if a substance meets the criteria for classification as dangerous in accordance with the Directive 2008/1272/EC (Directive 2008). Providing a MSDS is voluntary for substances which do not need to be classified in a system for their hazardous properties. However, each manufacturer has the legal obligation to guarantee the safe handling of the respective substance. For this reason, supplying a MSDS for newly synthesized nanomaterials with partly unknown hazardous properties is recommended.
- If a MSDS is not required according to article 32 of REACH, the supplier has nevertheless the duty to communicate information down the supply chain like the registration number (if available), details of any authorisation or restriction and any other available and relevant information about the substance.
- Further information is provided in several guidelines, for instance:
 - guidance on the compilation of safety data sheets (ECHA 2014)
 - Sicherheitsdatenblatt (SDB): Leitfaden für synthetische Nanomaterialien (SECO 2010)



Open cluster (left) and agglomerate with single fibres (right) of nanoscale material. Pictures were taken with a scanning electron microscope (SEM).

10 Additional protection measures for nanofibres

For handling nanofibres, **chapter 8** “Solubility of the nanomaterial: general protection measures for handling soluble powders” and **chapter 9** “Protection measures for dry, dusty nanomaterials” also apply. Chapter 10 provides additional and/or deviating protection measures. The recommendations are partly cited from the Announcement on Hazardous Substances 527 (AGS 2013).

10.1 Substitution

- Lower dust release: dry, dusty nanofibres can be dispersed in liquid media, bonded in permanent matrices or replaced by materials generating less dust (through moistening, granulates, pastes or premixed materials). The dust release can also be reduced by moistening the nanofibre powder. We recommend asking the manufacturer about the dustiness of the nanofibres.
- Fibre morphology: rigid fibres can be replaced by flexible ones. Fibres can be selected which are not biopersistent or rigid or which do not fulfil the WHO fibre criteria. We recommend asking the manufacturer about the fibre morphology.

10.2 Technical protection measures

- The work area should be structurally separated, e. g. a separate room. This place should not be a permanent workplace.
- It is recommended to use HEPA filters of class “H14” and/or devices which are approved for asbestos decontamination.

10.3 Organisational protection measures

- Open work process steps should be minimized as much as possible. Preferably, a closed system, for instance a glove box, should be used.
- If the closed system needs to be opened, local exhaust ventilation directly at the emission source is required.
- Surfaces can be cleaned by wet wiping or by using removable polymer films.

10.4 Personal protection measures

- Respiratory protection: the efficiency of a respirator mask depends upon, amongst other aspects, its tight fit. For nanofibres, half-face masks with a P3 particle filter are recommended if the concentration is above the detection limit (free release measurement for approval) (AGS 2013). The usage time of the respirator mask has to be restricted, taking into consideration the respective type of mask.
- If the activity lasts over a longer period of time, then power air purifying respirators (PAPR) with particle filter TM3P are recommended from an ergonomically point of view. The PAPR avoids an inhalation air resistance since the air flow is battery-driven and filtered prior to user respiration.
- Reusable protective suits should be cleaned regularly. Disposable protective suits should be disposed of at the end of the shift.

10.5 Effectiveness check

- A maximum limit for **fibre concentration** is recommended by DGUV: $< 10,000 \text{ fibres/m}^3$ (IFA 2012).
- The **minimum target** for protecting the workers is a fibre concentration below the acceptance limit $10,000 \text{ fibres/m}^3$.
- The **optimisation target** is to sustainably and reliably reduce the potential hazard from nanofibres before starting work to the background concentration (no increase during activity) or to the value of 500 fibres/m^3 (according to AGS 2007, withdrawal of protection measures (approval)). If the background concentration is higher than the value 500 fibres/m^3 , then the compliance with the background is regarded as sufficient.



Personal protection measures: schematic drawing of a power air purifying respirator (PAPR)



11 Instruction course, occupational health and toxicological advice

11.1 Instruction course

- The employer, respectively the managing director and immediate superior, are responsible for instructing personnel.
- The workers should be instructed regularly according to their place of work and their tasks (once before commencement of work, further training sessions at least once a year).
- The instruction course is a verbal instruction relating to the workplace or the activity.
- Effective educational and training materials should be developed for workers and occupational health professionals.
- The instruction course should include:
 - the specific physical and toxicological properties of the respective substances,
 - the need for special measures,
 - potential long term effects of aerosols, dusts and fibres,
 - information about occupational health and toxicological advice.
- The nature and extent of the instruction course should be adapted according to the risk at the workplace as well as to the qualification of the workers.
- The workers should actively participate in training, which includes sufficient possibilities for questions and feedback.
- There should be documentation of the instruction course signed by the participating workers.
- Relevant information should be included in the operating instructions.
- If contracted companies have tasks with possible contact with nanomaterials (for instance during cleaning), the customer has to ensure that the contracted company will be informed about potential hazards of nanomaterials and the rules of conduct before commencement of activities.

11.2 Occupational health and toxicological advice

- For all workers who handle hazardous substances, occupational health and toxicological advice should be discussed in the instruction course.
- Background knowledge concerning the respective toxic effect of the handled substances should be disseminated in order to promote workers' awareness and responsibility for their own health.
- Based on risk assessment, the employer decides if it is required to involve an occupational physician for this advice or if he/she, respectively a delegate, can carry out the occupational-medical and toxicological advice himself.
- Occupational physician and safety expert should cooperate closely in order to realise the occupational-medical and toxicological advice relating to specific on-site conditions.
- The involvement of the occupational physician in the occupational-medical and toxicological advice is recommended:
 - In case of high level of risk, for instance handling high amounts of rigid WHO-fibres (see **chapter 5.3**).
 - If the workers have need for advice concerning proposed or compulsory medical examinations according to national rules and practices in the case of work activities with hazardous substances.
 - If respiratory protection (mask with P2 or P3 particle filter) is used at the workplace.
- However, the presence of the occupational physician can be omitted if the hazardous properties of the substance are low and if the exposure is low or non-existent.
- In the framework of the occupational-medical and toxicological advice, the personnel should be informed about:
 - Potential exposure routes of the hazardous substances (in particular dermal, inhalative and – in individual cases – oral),
 - Possible effects and symptoms (acute, chronic) depending on the hazardous material,
 - Limitation of exposure by protective measures and personal hygiene,
 - Adequate protection measures, which they should implement for themselves and for their colleagues,
 - Preventive measures for safety and health at the workplace according to Directive 89/391/EC (Directive 1989), including health surveillance (see chapter 11.3),
 - The benefits offered by the health surveillance for the prevention of health disorders when applicable for a company,
 - The fact that workers can consult the occupational physician if they believe that there is a connection between their activity and a health disorder,
 - In this context, also the possibility that each worker can undergo a regular preventive occupational medical examination if requested according to the respective hazardous situation at the workplace.

11.3 Health surveillance

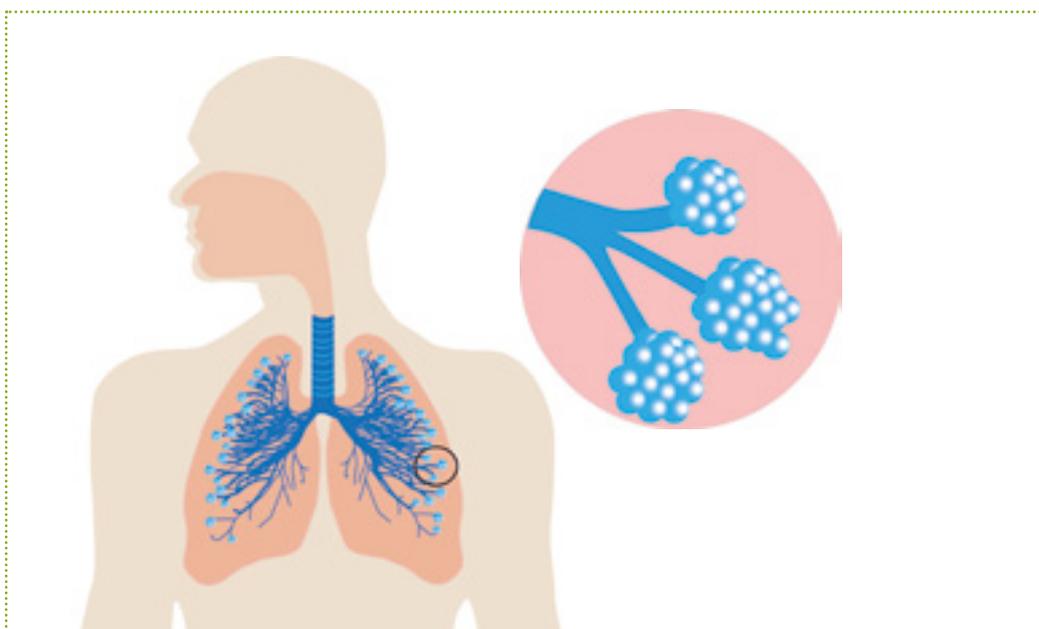
Health surveillance should be applied in the cases, where the results of the risk assessment reveal a high level of risk to the safety and health of workers. It complements the other specific protection, prevention and monitoring measures described above.

Health surveillance is not required if the results of the risk assessment show that there is only a slight risk to the safety and health of workers. This is, for instance, the case when the quantities of a hazardous chemical agent present in the workplace are small and the measures of prevention are sufficient to reduce that risk (Directive 1998).

Since there is no specific methodological program for health surveillance for exposure to nanomaterials, valid techniques of conventional occupational medical examinations can be used for health screening. Occasionally the health surveillance can be done as a counselling interview if clinical investigations are not necessary.

Health surveillance should be offered if:

- The workers have a need for occupational medical examinations in the case of work activities with several macro-scale hazardous substances (according to national rules and practices). If the nanoscale form of the substance is used, these occupational medical examinations are of course also required.
- Workers are exposed to nanomaterial-containing respirable dust at the workplace,
- Respiratory protection (mask with P2 or P3 particle filter) is used by the workers,
- The employer discovers that a worker suffers from temporary or permanent health problems.



Schematic illustration of the human respiratory tract and lung alveoli



12 Storage of nanomaterials

If unknown substances are handled, certain hazardous properties are assumed using a precautionary approach. For this reason, newly synthesized nanoparticles should be treated as if they would be acute toxic (Acute Tox. 3), irritant (Skin Irrit. 2), skin sensitising (Skin Sens. 1), or mutagenic (Muta. 2).

This precautionary approach applies unless sufficient information to the contrary is obtained, i. e. if certain conditions for relief can be matched.

The following recommendations for storage are partly cited from the control guidance sheets provided by the Federal Institute for Occupational Safety and Health (BAuA 2012):

- Define the storage area and vehicle traffic routes clearly. Put up clear signs.
- Ensure the area is spacious, organised, well lit and ventilated.
- Label all containers, including opened ones.
- If the nanomaterial is newly synthesized and if the hazardous properties are (partly) unknown, it should be highlighted that the handled substance is nanoscale, respectively that it still has partially unknown properties. For this reason it is recommended to e. g. add the phrase “Attention – substance not yet tested completely” additionally to the label of the already known properties from classification.
- Store chemicals that react readily together in separate cabinets.
- Ask your chemical supplier for specific advice on which chemicals to store separately from others.
- When combustible powders or liquids are stored, it is recommended to observe specific requirements for fire and explosion protection. In their dry state, certain nanoparticles can constitute an explosion risk that is far greater than the same microscale material.
- Collect paper, wipes, PPE and other items with loosely adhering particles in a plastic bag or other sealable container stored in the laboratory hood. When the bag is full, close it and carefully place it into a second plastic bag or other sealable container, avoiding outside contamination. Take it out of the hood and label the outer bag with an appropriate waste label.



13 Disposal Procedures

The waste management guidance for the disposal of hazardous materials applies to nanomaterial-bearing waste streams (solid and liquid waste), including:

1. pure nanoparticles and nanoparticles containing waste products
2. items contaminated with nanoparticles, such as containers, wipes, biological tissues, culture wares and disposable PPE
3. liquid suspensions containing nanoparticles.

The following recommendations for disposal procedures are given:

- A plan for storage and disposal of nanoparticles or nanoparticles contaminated waste should be developed, taking into account the hazardous nature of the particles and the quantities involved.
- Material from nanoparticle-bearing waste streams should not be put into the household waste or flushed down the drain.
- Equipment used during nanoparticle handling should be decontaminated before it is disposed of or reused. Waste resulting from decontamination should be treated as nanoparticle-bearing waste.

13.1 Waste disposal

- Nanomaterials for removal should be collected within a labelled, closed container, for instance a drum with a standard lid and clamping ring. If the hazardous properties of the newly synthesized nanomaterial are partially unknown, it is recommended to highlight this on the container for instance with the phrase "Attention – contains waste of a substance not yet tested completely". This also applies to filter waste.
- If you are unsure about the correct waste disposal, you are advised to consult the disposal company.
- The disposal should be in line with the substance-specific criteria and according to the AVV- keys of the European list of waste.
- The respective hazardous properties of the substance should be taken into account.

14 Sample letter for questions addressed at a manufacturer

Dear manufacturer / distributor,

We would like to ask you about a potential hazard regarding handling of your product XXX. For assessing the risk, we require the following information: has this product been tested for the following hazardous properties:

- acute toxicity (Acute Tox. 3)
- irritation (Skin Irrit. 2)
- skin sensitization (Skin Sens. 1)
- mutagenicity (Muta. 2)

Does this classification refer specifically to the nanoscale form of your product?

In addition if fibres are handled:

Furthermore, we need the certain morphological information: is the fibre is longer than 5 μm and the length-diameter-ratio higher than 1:3, are they rigid and friable or flexible?



15 Conclusions

This guideline on good working practices concerning nanomaterials is suitable for use by research institutions as well as SME industries. It provides four decision criteria that assist in performing an adequate risk assessment and in deriving appropriate occupational safety measures.

These criteria evaluate

1. the **physical condition** of the nanomaterial (present in matrix, liquids or as powder),
2. the **water solubility**,
3. if the nanomaterial is a **fibre** according to WHO criteria and
4. if the materials' toxicology is chemically mediated on its microscale form.

According to the decision criteria, safety strategy levels tailored to the respective groups of nanomaterials can be derived. The safety strategy considers the precautionary approach and follows the priority list of the STOP principle: substitution, technical measures, organisational measures and personal protection measures.

The occupational safety measure recommendations are differentiated according to the following groups of nanomaterials: for handling nanomaterials

1. bound in a **matrix**,
2. dissolved in a **liquid**,
3. **soluble powders**,
4. dry and **dusty nanoparticles** and
5. **fibrous** in nature.

The recommendations are supplemented by sections on transport and market placement, explosion protection, effectiveness check of the protective measures, training, occupational health advice, storage and disposal.

The pathway from decision criteria to the appropriate safety strategy level is visualised by a flow chart. This guideline is based on a document with the intention to provide guidance for partner laboratories which were synthesizing, testing and measuring nanomaterials in order to develop reference methods and materials.



16 References

AGS 2007, Committee on Hazardous Substances – AGS, **Abbruch-, Sanierungs- oder Instandhaltungsarbeiten / Asbestos: Demolition, reconstruction or maintenance work**. Technical Rules for Hazardous Substances TRGS 519, Joint Ministerial Gazette, January 2014. Available from: www.baua.de/de/Themen-von-A-Z/Gefahrstoffe/TRGS/TRGS-519.html [accessed 08 December 2014]. *(mandatory and up-to-date is the German version)*

AGS 2008a, Committee on Hazardous Substances – AGS, **Laboratorien / Laboratories**. Technical Rules for Hazardous Substances TRGS 526, Joint Ministerial Gazette, February 2008. Available from: www.baua.de/de/Themen-von-A-Z/Gefahrstoffe/TRGS/TRGS-526.html [accessed 08 December 2014].

AGS 2008b, Committee on Hazardous Substances – AGS, **Schutzmaßnahmen / Protection measures**. Technical Rules for Hazardous Substances TRGS 500, Joint Ministerial Gazette, May 2008. Available from: www.baua.de/de/Themen-von-A-Z/Gefahrstoffe/TRGS/TRGS-500.html [accessed 08 December 2014].

AGS 2010, Committee on Hazardous Substances – AGS, **Risk Assessment for Activities involving Hazardous Substances**. Technical Rules for Hazardous Substances TRGS 400, Joint Ministerial Gazette, December 2010, Available from: www.baua.de/en/Topics-from-A-to-Z/Hazardous-Substances/TRGS/TRGS-400.html [accessed 08 December 2014].

AGS 2013, Committee on Hazardous Substances – AGS, **Manufactured Nanomaterials**. Announcement on Hazardous Substances 527, Joint Ministerial Gazette, Mai 2013, Available from: www.baua.de/en/Topics-from-A-to-Z/Hazardous-Substances/TRGS/pdf/Announcement-527.pdf [accessed 29 August 2014].

AGS 2014, Committee on Hazardous Substances – AGS, **Arbeitsplatzgrenzwerte / Occupational exposure limit values**. Technical Rules for Hazardous Substances TRGS 900, Joint Ministerial Gazette, October 2013, Available from: www.baua.de/de/Themen-von-A-Z/Gefahrstoffe/TRGS/TRGS-900.html [accessed 08 December 2014]. BAuA 2012, Federal Institute for Occupational Safety and Health (BAuA), **Schutzleitfäden / Control guidance sheets**, Available from: www.baua.de/de/Themen-von-A-Z/Gefahrstoffe/EMKG/Schutzleitfaeden.html [accessed 19 July 2012].

BAuA-VCI 2012, Federal Institute for Occupational Safety and Health (BAuA) and German Chemical Industry Association (VCI), **Empfehlung für die Gefährdungsbeurteilung bei Tätigkeiten mit Nanomaterialien am Arbeitsplatz**, May 2012, Available from: www.baua.de/de/Publikationen/Fachbeitraege/Gd4.html [accessed 19 July 2012].

BG Bau 2012, German insurance association for the construction industry (BG Bau), **Nano-Liste der BG BAU – Nanoteilchen in Bau- und Reinigungsprodukten**, Available from: www.bgbau.de/praev/fachinformationen/gefahrstoffe/nano/index [accessed 19 July 2012].

DGUV 2008, Statutory employment accident insurance fund for the Chemical Industry (BG Chemie) / German Social Accident Insurance (DGUV), **Working Safely in Laboratories**, Jedermann-Verlag, 2008.

Directive 1989, 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**, 1989, Available from: <http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CELEX:31989L0391:en:HTML> [accessed 09 August 2012].

Directive 1992, Directive 92/58/**EEC of 24 June 1992 on the minimum requirements for the provision of safety and/or health signs at work (ninth individual Directive within the meaning of Article 16 (1) of Directive 89/391/EEC)**, 1992, Available from: <http://osha.europa.eu/de/legislation/directives/workplaces-equipment-signs-personal-protective-equipment/osh-directives/9> [Accessed at 15 August 2012]

Directive 1994, Directive 94/9/**EC of the European Parliament and of the Council of 23 March 1994 on the approximation of the laws of the Member States concerning equipment and protective systems intended for use in potentially explosive atmospheres (OJ L 100, 19.4.1994)**, 1994, Available from: <http://ec.europa.eu/enterprise/sectors/mechanical/documents/legislation/atex/> [accessed 09 August 2012].

Directive 1998, Council Directive 98/24/**EC of 7 April 1998 on the protection of the health and safety of workers from the risks related to chemical agents at work (fourteenth individual Directive within the meaning of Article 16(1) of Directive 89/391/EEC)**, 1998, Available from: <http://eurlex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:1998:131:0011:0023:EN:PDF> [accessed 10 August 2012]

Directive 1999, **Directive 1999/92/EC of the European Parliament and of the Council of 16 December 1999 on minimum requirements for improving the safety and health protection of workers potentially at risk from explosive atmospheres (15th individual Directive within the meaning of Article 16(1) of Directive 89/391/EEC)**, 1999, Available from: <http://eurlex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2000:023:0057:0064:en:PDF> [accessed 09 August 2012].

Directive 2008, **Regulation (EC) No 1272/2008 of the European Parliament and of the Council of 16 December 2008 on classification, labelling and packaging of substances and mixtures, amending and repealing Directives 67/548/EEC and 1999/45/EC, and amending Regulation (EC) No 1907/2006**, 2008, Available from: <http://eurlex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2008:353:0001:1355:en:PDF> [accessed 09 August 2012].

ECHA 2014, European Chemicals Agency, **Guidance on the compilation of safety data sheets**, version 2.1, 2014, Available from: http://echa.europa.eu/documents/10162/13643/sds_en.pdf, 2014 [accessed 04 March 2015].

EU-OSHA 2012, **The risks of the very small**, News release, 20.06.2012, Available from: http://osha.europa.eu/en/press/press-releases/risks_of_very_small [accessed 19 July 2012].

GHS 2008, **EU Regulation (EC) No 1272/2008 on Classification, Labelling and Packaging of Substances and Mixtures, (introduces the Globally Harmonised System of the United Nations for the classification and labelling of chemicals (GHS) into the EU)**, 2008, Available from: <http://echa.europa.eu/web/guest/regulations/clp/legislation> [accessed 19 July 2012].

HVBG 2006, Federation of Institutions for Statutory Accident Insurance and Prevention (HVBG), **Schutzmaßnahmenkonzept für Spritzlackierarbeiten – Lackaerosole**, BG-Regel 231, January 2006, Available from: www.bgbau-medien.de/zh/bgr231/titel.htm [accessed 08 December 2014].

IFA 2012, **Institute for Occupational Safety and Health of the German Social Accident Insurance**, Available from: www.dguv.de/ifa/de/fac/nanopartikel/beurteilungsmasstaebe/index.jsp [accessed 19 July 2012].

Poland, C. A., Duffin, R., Kinloch, I., Maynard, A., Wallace, W. A. H., Seaton, A., Stone, V., Brown, S., MacNee, W. and Donaldson K., 2008, **Carbon nanotubes introduced into the abdominal cavity of mice show asbestos-like pathogenicity in a pilot study, nature nanotechnology**, Volume 3, 2008.

SECO 2010, State Secretariat for Economic Affairs, **Sicherheitsdatenblatt (SDB): Leitfaden für synthetische Nanomaterialien**, 2011, Available from: www.arbeitsinspektion.gv.at/NR/rdonlyres/8ED7A8DD-4F25-46C8-A939-5B544BE8922E/0/CH_Nano_SDB_Leitfaden_Bez_2010.pdf [accessed 13 August 2012]

VdL 2012, German association of the coatings and printing ink industries, **Statement zum SRU-Gutachten**, Available from: www.lackindustrie.de [accessed 19 July 2012].

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