The Committee on Hazardous Substances (AGS) will regularly adapt the Announcement on Hazardous Substances 527 (BekGS 527) to the state of knowledge. Hints from practice, especially according to risk assessment, protective measures according to the state of the art and effectiveness checks are welcome: AGS-management board, BAuA, Postfach 17 02 02, 44061 Dortmund or E-mail: ags@baua.bund.de.

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Announcements on Hazardous Substances	**Manufactured Nanomaterials**	**Announcement 527**

The Announcements on Hazardous Substances reflect the state of the art, the state of occupational health and occupational hygiene as well as other sound work-scientific knowledge relating to activities involving hazardous substances including their classification and labelling. The

Committee on Hazardous Substances (AGS)

compiles or adapts the rules, and they are announced by the Federal Ministry of Labour and Social Affairs (BMAS) in the Joint Ministerial Gazette (GMBl).

Contents

1 Scope and objectives of the Announcement

(1) The objective of the present Announcement is to give recommendations for the protection of the safety and health of employees at the workplace during activities involving substances or mixtures[1] or articles consisting of or containing manufactured nanomaterials. The basis for the present Announcement is the recommendation of the European Commission on the definition of the term ‘nanomaterial‘ [1]. Natural and incidental nanomaterials are not considered in the present Announcement. Likewise, the present Announcement does not address aspects of the risk assessment, when such material is used by consumers.

(2) A substance or a mixture consisting of or containing manufactured nanomaterials shall not be generally regarded as a dangerous substance or a hazardous substance as defined in the Ordinance on Hazardous Substances (Gefahrstoffverordnung, GefStoffV). The risk assessment of manufactured nanomaterials requires a differentiated consideration based on the properties of the respective manufactured nanomaterial and the activities performed.

(3) Currently, uncertainties persist in characterising the associated risk, and the insufficient possibilities for determining exposure may lead to a lack of clarity in assessing the risk and differentiating between the occupational safety and health measures to be derived from such a risk.

(4) The present Announcement complements the Technical Rules for Hazardous Substances with regard to the risks caused by manufactured nanomaterials, and particularly the Technical Rule for Hazardous Substances (TRGS) 400 on the “Risk Assessment for Activities involving Hazardous Substances” and the TRGS 402 on the “Identification and Assessment of the Risks from Activities involving Hazardous Substances: Inhalation Exposure”. The character of the Announcement is that of a conceptual guidance and it contains more specific guidelines for action wherever necessary and possible.

(5) In the context of risk assessment, all exposure routes shall be taken into account. According to the view of the Committee on Hazardous Substances (AGS), in this study the inhalation exposure to manufactured nanomaterials shall be primarily investigated. For inhalation exposure, it is necessary to assess the exposure effects both with regard to the dust/particle fraction and to liquid aerosols

1. consisting of nano-objects or containing nano-objects, and
2. consisting of or containing non-nanoscale aggregates or agglomerates of nano-objects [3].

(6) The risk caused by absorption through the skin or swallowing is considered to be of no outstanding significance. Swallowing can be avoided by targeted hygiene measures. Protective measures against skin contact may be derived in line with the TRGS 401 “Risks resulting from skin contact -identification, assessment, measures” by considering the substance property, the effective area and the duration of the exposure. Furthermore, the information on protective gloves in Section 4.4.4 shall be respected.

[1] In this Announcement, the terms ‘mixture’ (pursuant to Regulation (EC) No. 1272/2008, or the “CLP Regulation”) and ‘preparation’ (pursuant to Directive 1999/45/EC, or the “Dangerous Preparations Directive”) are used synonymously.

(7) The scope of the assessment includes all workplaces along the value chain where activities are performed with manufactured nanomaterials. They include research and development, production, industrial and manual processing and treatment as well as disposal. They shall also cover activities such as cleaning, servicing, maintenance and repair work.

2 Definitions

(1) There is no uniform and legally binding definition of the term ‘nanomaterial’. The European Commission recommends that not only manufactured nanomaterials but also natural or incidental nanomaterials containing unbound particles as well as aggregates or agglomerates shall be designated as nanomaterials, when they correspond to the additional criteria listed in the above-mentioned recommendation [1]. In its recommendation, the European Commission does not distinguish between established and new materials which - according to the proposed definition - are now summarily designated as manufactured nanomaterials.

(2) Solid manufactured nanomaterials according to the recommendation of the European Commission on a definition of nanomaterials [1] as well as liquid mixtures containing such materials are in the focus of the present Announcement, when they are

1. used as aerosols in normal operation or during regular use, or
2. are agitated again and therefore may form aerosols in the air at the workplace.

In this context, the consideration of liquid mixtures containing manufactured nanomaterials exceeds the above-mentioned recommendation by the European Commission.

(3) The total material may be present either as one substance or as a mixture. When it consists of a substance, it may exclusively consist of nano-objects and their non-nanoscale aggregates and agglomerates, or it may only contain parts of them. In case of a mixture, it may consist of nano-objects and their non-nanoscale aggregates and agglomerates as well as other ingredients. The European Commission defines material as a nanomaterial, when it contains unbound particles in the form of aggregates or agglomerates and when 50% or more of the particles in the size distribution count show one or more external dimensions in the size range from 1 nm to 100 nm [1]. It shall be taken into account that the particle size distribution of the total material may change in processing stages such as dispersing.

(4) Nano-objects are materials of one or more external dimensions (length, width, height) of approx. 1 to 100 nm. They are present as nanoparticles, nanofibres or nanoplates.

(5) The term “microscale” is used as a differentiation from the term “nanoscale”. Consequently, the microscale range of 100 nm and above follows after the nanoscale range.

(6) An agglomerate consists of nano-objects or aggregates or of a mixture of nano-objects and aggregates held together by weak interactions. Its external surface corresponds approximately to the aggregated surfaces of its individual components.

(7) An aggregate consists of nano-objects which are held together by strong bonding forces or which are fused. Its external surface may be significantly smaller than the aggregated surfaces of its individual components.

(8) The biopersistence of nanomaterials describes their property to dissolve in pulmonary or tissue fluid. Biopersistence will decrease with increasing dissolution rates.

(9) The solubility in water is pragmatically used in this Announcement as a criterion to assess biopersistence. For the purposes of this Announcement, nanomaterials with a solubility in water of less than 100 mg/l are practically insoluble and therefore bio-persistent. As a consequence, nanomaterials with a water solubility above 100 mg/l are regarded as soluble. When findings are available on the solubility of nanomaterials in biological media, these shall be primarily used for the assessment of biopersistence.

(10) The term ‘GBP nanomaterials’ (granular biopersistent particles) is used for particulate solids which fulfil the criteria for granular biopersistent particles (GBP) and also conform to the definition for nanomaterials in this Announcement. Fibrous nanomaterials will normally not be classified as ‘GBP nanomaterials’.

(11) The term ‘difference in potency’ describes the fact that a nanoscale material might have a stronger health effect than the same mass of the same material in microscale form. For preventive reasons and in case of GBP nanomaterials, this possibility is taken into account by an estimated potency factor (see Section 4.2.3 para. 3).

(12) Rigid fibres are considered to be fibres which will not twist or intertwine, neither with themselves nor with other fibres.

(13) According to Section 2.3 para. 1 of the TRGS 905, the “Directory of carcinogenic, mutagenic or reproduction toxic substances” (Verzeichnis krebserzeugender, erbgutverändernder oder fortpflanzungsgefährdender Stoffe), WHO fibres are characterised by a length of > 5 µm, a diameter of < 3 µm and a length-to-diameter ratio of > 3:1.

(14) Furthermore, this Announcement uses terms in the manner, in which they are defined in the glossary of terms included in the rules of the German Ordinance on Industrial Safety (Betriebssicherheitsverordnung, BetrSichV), the Biological agents Ordinance (Biostoffverordnung, BioStoffV) and the Ordinance on Hazardous Substances (Gefahrstoffverordnung, GefStoffV) issued by the Advisory Committee on Protection at Work (Ausschuss für Betriebssicherheit, ABS), the Committee on Biological Agents (Ausschuss für biologische Arbeitsstoffe, ABAS) and the Committee on Hazardous Substances (Ausschuss für Gefahrstoffe, AGS) [4].

3 Information gathering

The employer shall determine whether employees perform activities with manufactured nanomaterials or whether such nanomaterials are released. These activities shall be taken into account for gathering information and assessing the risk and for developing protective measures.

3.1 Information sources

(1) In particular the safety data sheet is used as a source of information in the industrial and commercial supply chain. It should contain the information whether the substance or the mixture consists of or contains manufactured nanomaterials.

(2) The following sections of the safety data sheet (SDS) should yield specific information on manufactured nanomaterials:

1. Section 1: Identification of the substance/mixture and of the company.
2. Section 2: Hazards identification
3. Section 3: Composition/information on ingredients
4. Section 9: Physical and chemical properties

In particular, Sections 3 and 9 should include information on the presence of nanomaterials. In Section 9, the “appearance” information and the physical state being listed as “solid” should include a reference to a nanomaterial [5].

(3) The compilation and communication of safety data sheets is mandatory only for substances and mixtures, which are classified as hazardous. In the chemical industry, it is customary, however, to provide safety data sheets also for substances and mixtures, which are not classified as hazardous [6]. For substances and mixtures consisting of or containing manufactured nanomaterials, safety data sheets should therefore be available.

(4) Technical Data Sheets or additional product information (such as advertising brochures) may also contain references to the presence of manufactured nanomaterials in the substance or the mixture in question.

(5) Information on construction or cleaning products, which are advertised as containing nanomaterials or which use nanotechnological properties, are available in the ‘nanolist’ of the German Social Accident Insurance Institution for the building trade (Berufsgenossenschaft der Bauwirtschaft) [7].

(6) Information on the ingredients of articles may be available through industry-specific data sheets (such as the IMDS (International Material Data System) in the automotive industry or IEC/PAS 61906 in the electronics industry).

(7) In case of ingredients, which are normally present in nanoscale form, it is possible to contact the supplier in case of activities involving dust generation or in case of information deficits. Using a letter of the format included in Appendix 1 is recommended for this purpose.

3.2 Substance-specific information

(1) In case of substances or mixtures consisting of or containing manufactured nanomaterials, the following information may be relevant for identifying manufactured nanomaterials and assessing the associated risk and shall be taken into account in the risk assessment, whenever it is available:

1. classification of the nanoscale form,
2. particle size distribution (such as granulometric findings),
3. the specific surface,
4. information regarding the form and structure (such as information on the applicability of the WHO fibre criteria),
5. surface modification,
6. solubility in water (on the assessment of biopersistence see Section 4.2 paras. 3 to 5),
7. data on dustiness (such as characteristics of dust),
8. combustion data (such as flammability and explosion limits).

With regard to the analysis of the particle size distribution in the total material, however, a generally recognised method is not available yet. And methods to determine the dusting index, which may be used to describe the dustiness, have not yet been developed specifically for manufactured nanomaterials. As long as recognised methods are not available, the best available alternative methods should be used.

(2) When not even the minimum information on solubility in water (see Section 4.2 para. 3) as well as form and structure (see Section 4.2.4) is available, an enquiry should be forwarded to the manufacturer. This may be done with the type of letter included in Appendix 1.

(3) In case of biopersistent, rigid, fibrous nanomaterials in conformity with the WHO fibre criteria, or when no morphological tests are available for biopersistent fibrous nanomaterials, such fibres shall be preventively treated as substances with potentially carcinogenic properties.

(4) In the context of the substance registration pursuant to Regulation (EC) No. 1907/2006 (REACH), all applications of a substance, i.e. including those of the nanoscale form, shall be assessed. Even though there is no obligation to characterise nanomaterials using specific test programmes, this is recommended in the REACH guidance issued by the European Chemicals Agency (ECHA). The appropriate substance-specific information may be downloaded from ECHA, when such tests have been performed [8].

3.3 Information gathering - activities

(1) The probability of a release of nano-objects and their aggregates or agglomerates depends on the releasing source and the activity performed.

(2) With decreasing probability, they may be released during

1. manufacture and especially the gaseous phase synthesis [9] and in so-called “top-down” processes, when nano-objects are produced by mechanically crushing the original material in a milling process. An exposure of employees during the manufacturing process may occur especially at interfaces such as the filling stage, during sampling, cleaning and maintenance activities and in case of fault of the specified normal operation. In contrast, the probability of release must be

regarded as low for manufacturing processes in the liquid phase such as precipitation processes.

2. processing of solids or mixtures (powders and granulates or flakes) consisting of or containing manufactured nanomaterials during activities such as weighing, mixing, dosing, packaging and mechanical finishing. In such cases, the probability of release depends on the dusting properties of the solid matter and the type of activity.

3. processing and treatment of solid articles containing manufactured nanomaterials bonded to a matrix such as the cutting or grinding of polymers or varnishlayers with embedded nanomaterials. It is the subject of on-going studies to what extent the nanomaterial used is re-released from the matrix in particulate form. Studies on the sanding process of varnish systems containing manufactured nanomaterials show, however, that particles of less than 100 nm are released, but it was not observed that nanoparticles added to the varnish were released from the binder matrix [10]. When articles containing biopersistent fibrous nanomaterials are abraded (see Section 4.2.4), preventively a potential release of these fibres must be assumed, unless sufficient knowledge is available to exclude such a release.

4. processing of mixtures containing manufactured nanomaterials bonded in a liquid matrix (including pastes or sludges). For activities involving liquid media, inhalation will normally be excluded, if aerosol formation is avoided [9]. For industrial applications and the manual processing of liquid varnishes and paints, studies show that nanoparticles do not escape from such media [11]. But other processes involving aerosol formation or other mixtures have not yet been sufficiently studied to fully exclude a release of nanoparticles.

(3) One source of information for the processing stage is the safety data sheet. Its Section 3 should also contain information on the presence of nanomaterials for specified uses (such as the indication that spraying will generate aerosols containing nanoparticles). And the statement that no nano-objects will be released during specified uses should also be found in this Section.

(4) The extended safety data sheet for substances includes exposure scenarios [12] for specified uses and will also contain the appropriate protective measures to control health and environmental hazards.

(5) When measured values are available on the exposure to alveolar dust (the alveolar dust fraction) during operation or at comparable workplaces, this information may also be included in the risk assessment (see Section 4.3 para. 6).

3.4 Information gathering – assessment criteria

(1) Assessment criteria for the exposure findings may include, for example:

1. legally binding, health-based limit values or exposure-risk relationships,

2. expert proposals for limit values such as the proposals of the Senate Commission for the Investigation of Health Hazards of Chemical Compounds in the Work Area (Senatskommission zur Prüfung gesundheitsschädlicher Arbeitsstoffe, or MAK (Maximum Concentration at the Workplace) Commission) or

other scientific expert commissions (such as foreign limit values or proposed limit values),

3. preliminary corporate internal observation or action levels, which the employer determines on the basis of reliable data in the context of its own risk assessment,
4. DNEL values (Derived No Effect Level) which were derived by the industrial manufacturer in the context of a REACH registration and stated in the safety data sheet, for example [12] or
5. the Benchmark Level Concept developed by the Institute for Occupational Safety and Health of the German Social Accident Insurance (Institut für Arbeitsschutz der DGUV, IFA)) [13].

(2) At present, there are no legally binding occupational exposure limit values for manufactured nanomaterials. As a minimum, compliance shall be assured with the occupational exposure limit value for the respirable and the alveolar dust fraction as well as the substance-specific limit values (see Section 4.5.1).

(3) Previously published recommendations for assessment criteria for manufactured nanomaterials are presented in Appendix 2 and may be used after an appropriate assessment by experts.

4 Risk assessment

4.1 Procedure

(1) The risk assessment shall be performed in line with the principles set out in the TRGS 400.

(2) In addition, the assessment of the risk caused by manufactured nanomaterials shall be performed on the basis of the information gathered according to Section 3. It forms the basis for the determination of protective measures.

(3) For preventive reasons, a risk shall always be assumed for activities involving dust-generating nanomaterials. Its level shall be derived from the risk assessment.

(4) Normally, the risk caused by nanomaterials will decrease along the value chain, when the nanomaterials are bound for downstream uses in a matrix such as varnish, for example.

(5) A flowchart is included in Appendix 3 as guidance for identifying activities, for which measures according to §§ 7 and 8 of the Ordinance on Hazardous Substances (GefStoffV) will suffice (see Section 4.3 para. 3).

4.2 Assessment of health hazards

(1) When assessing the health effects of manufactured nanomaterials, a minimum assessment shall consider

1. its effect based on its specific chemical composition (based on its classification, for example) and
2. its effect based on its characterisation as a “biopersistent nano-object” irrespective of its specific chemical composition.

(2) Based on its toxicological properties, form and structure as well as its biopersistence, nanomaterials can be classified as follows:

1. soluble nanomaterials,
2. biopersistent nanomaterials with specific toxicological properties,
3. biopersistent nanomaterials without specific toxicological properties (GBP nanomaterial),
4. biopersistent fibrous nanomaterials.

For some forms of nanomaterials, a clear classification in one of these groups is not yet possible. They include graphene flakes, for example. In specific cases, coatings and charges of the surface of nano-objects may influence the health effect, and nanomaterials without specific toxicological properties may become specifically toxic, for example after coating [14]. When the surface is modified, the toxicological properties must be analysed specifically for each case.

(3) Solubility in water may be used as a yardstick for biopersistence. With good water solubility, a good solubility in biological media may normally be assumed. But this does not apply across the board. In individual cases, poor solubility in water may nonetheless be associated with good solubility in biological media. Metallic cobalt, for example, is not soluble in water, but it shows good solubility in serum.

(4) Internationally, there is no uniform definition of concentration ranges to describe solubility in water. A uniform European determination of water solubility has been defined in the European Pharmacopoeia [15]. The Announcement refers to this determination, which is also used in GESTIS, the Hazardous Substance Database of the German Social Accident Insurance. We therefore propose to apply the following differentiation for solubility:

1. substances with a water solubility of less than 100 mg/l are “practically insoluble”,
2. in contrast to the European Pharmacopoeia, this Announcement regards substances with a water solubility of more than 100 mg/l as soluble without any further differentiation.

(5) The distinction between ‘soluble’ and ‘practically insoluble’ was also made considering the solubility of amorphous silicon dioxide (CAS no. 7631-86-9). Based on its solubility (solubility in water: 120 mg/l), this substance does not show the typical GBP effects. According to this classification, most manufactured nanomaterials tested in the toxicological test programme of the OECD Working Party on Manufactured Nanomaterial are considered as practically insoluble [16].

4.2.1 Soluble nanomaterials

When the material exclusively consists of soluble nano-objects, the risk assessment shall be performed in accordance with the TRGS 400. Materials in this substance

category are for example certain soluble salts containing nanoparticles (such as sodium chloride nanoparticles) or amorphous silicon dioxide.

4.2.2 Biopersistent nanomaterials with specific toxicological properties

(1) The assessment of the health hazards caused by biopersistent nanomaterials will focus on their specific toxicological property as derived from their chemical composition, when

1. such nanomaterials show properties which are harmful to human health, or
2. the microscale form of these materials has toxic properties, and when no data to the contrary are available for the nanoscale form.

Biopersistent nanomaterials with specific toxicological properties are for example gold, silver or zinc oxide.

(2) It must be considered during the assessment that, in comparison to coarser particles, the bioavailability of nanomaterials may be higher due to their larger specific surface. As a consequence, protective measures shall be taken in accordance with Section 4.4.

(3) For those microscale substances, which may be present as nanomaterials with specific toxicological properties, there are substance-specific occupational limit values or other assessment criteria for the alveolar or the respirable dust/particle fractions. They include maximum workplace concentrations as well as SCOEL proposals. These values normally are less than 0.1 mg/m³ (see Section 4.5.1 para. 2).

4.2.3 Biopersistent nanomaterials without specific toxicological properties (GBP nanomaterials)

(1) Biopersistent nanomaterials without specific toxicological properties and without fibrous structures (GBP nanomaterials) do not show any substance-specific toxicity over and beyond their particulate effect. Materials in this substance category are carbon black, titanium dioxide, aluminium oxide and aluminium silicate, for example. They used to be called “inert substances” in the past.

(2) When assessing the health hazards of these GBP nanomaterials, the focus is on a potential chronic danger to human health after respiration [17]. For the designation of protective measures, it shall therefore be assumed that the toxicological effect of nanomaterials corresponds at least to the alveolar dust fraction (the ‘A’-dust fraction), when mass concentrations are considered.

(3) When assessing the exposure to GBP nanomaterials, the assessment criteria according to Section 3.4 para. 1 nos. 1 to 4 may be used. When there are no assessment criteria according to. Section 3.4 para. 1 nos. 1 to 4 and when Section 3.4 para. 1 no. 5 does not apply, it is proposed on the basis of basic research findings that a potency differentiating factor of 2 shall always be taken into account for GBP nanomaterials [18]. Therefore, the assessment criterion results in the amount of half of the occupational limit value (in relation to the currently valid and legally binding occupational limit value for the alveolar dust fraction laid down in the TRGS 900). The

assessment criterion for assessing the occupational exposure should not be higher than 0.5 mg/m^3 (at a density of 2.5 g/cm^3).

4.2.4 Biopersistent fibrous nanomaterials

(1) Biopersistent nanomaterials with a fibrous, rigid structure - so-called nanofibres or nanotubes - fulfilling the WHO fibre criteria, may show an effect similar to asbestos. Materials in these substance categories include certain types of carbon nanotubes, for example.

(2) It is only possible to assume that biopersistent fibrous nanomaterials do not have properties similar to asbestos, if the manufacturer has proven this fact for his respective product or is able to present evidence that the fibres do not fulfil the WHO fibre criteria.

4.3 Risk identification

(1) In case of substances or mixtures or articles consisting of, or containing manufactured nanomaterials, their inhalation exposure must be assessed in particular. The level of the risk caused by manufactured nanomaterials primarily depends on the

1. associated hazard characteristics (considering its solubility in water or biological media and the information on its form and structure),
2. type of use,
3. dustiness properties, and
4. working conditions.

In order to determine suitable and appropriate protective measures, this information and the results of exposure studies may result in an assessment saying that measures according to §§ 7 and 8 of the Ordinance on Hazardous Substances (GefStoffV) will suffice (see flowchart in Appendix 3). On the significance of hazards caused by swallowing or skin contact, see Section 1 para. 6.

(2) When manufactured nanomaterials are handled under normal laboratory conditions, the protective measures laid down in the TRGS 526 “Laboratories” shall apply. Normal laboratory conditions are described in Section 3.3.3, and the minimum protective measures to be implemented in case of new and not yet sufficiently studied substances are found in Section 3.1 para. 5 of the TRGS 526. Information on additional protective measures for activities involving nanomaterials in laboratories is also available from the Laboratories Working Party (AK Laboratorien) of the German Social Accident Insurance (DGUV) [19].

(3) For the following activities, measures according to §§ 7 and 8 of the Ordinance on Hazardous Substances (GefStoffV) are considered as sufficient:

1. activities involving soluble nanomaterials without specific toxicological properties,
2. activities involving nanomaterials bonded to solids (articles, for example) and for which a release of the nanomaterials from the matrix can be excluded, or

3. activities involving nanomaterials, for which the presence of respirable workplace aerosols can be excluded on the basis of their type of application or the process involved (e.g. when using liquid formulations without a spray application).

(4) Agglomerates may disperse more easily than aggregates as a result of shearing forces or the presence of aqueous solutions. A release of nano-objects from aggregates is considered to be unlikely due to permanent chemical bonding. It has not yet been sufficiently studied to what extent agglomerates and possibly aggregates may degrade to form nano-objects in the human body. As no conclusive statements can be made on this subject at this time, aggregates and agglomerates shall also be considered in the risk assessment.

(5) For activities involving biopersistent, rigid, fibrous nanomaterials corresponding to the WHO criteria, an asbestos-type effect shall be assumed for preventive reasons. The discussion on the assessment of flexible biopersistent fibres has not been concluded. For such substances, an analysis must be performed for each specific case (see also Section 4.2.4).

(6) When the criteria according to para. 3 nos. 1 to 3 do not apply, either in full or in part, a decision shall be taken to what extent additional protective measures must be introduced in accordance with §§ 9 and 10 of the Ordinance on Hazardous Substances (GefStoffV), or whether dust-reducing measures pursuant to Annex I no. 2 of the Ordinance on Hazardous Substances (GefStoffV) must be taken. To determine additional protective measures, an approximate determination of employee exposure may be used. When appropriate findings from exposure studies are available, it is not necessary to introduce additional protective measures. Findings to be used for this purpose may be results of A-dust measurements or particle number concentration measurements in line with Section 4.5.

(7) For the abrasive treatment of a matrix containing permanently bonded nano-objects (such as varnishes), it may normally be assumed that nano-objects are not released. For biopersistent fibrous nanomaterials (see Section 4.4.2 para. 7 on this topic), an analysis shall be made for each case. But other alveolar dusts may possibly be generated of which the risks must be assessed and minimised.

4.4 Deriving protective measures

(1) When deriving protective measures for manufactured nanomaterials with specific toxicological properties, such protective measures shall be guided by the classification of the total material, unless a classification of the nanomaterial is available.

(2) When no findings are available on the classification of the total material, the protective measures shall be derived, as if the properties according to the TRGS 400 Section 4.2 para. 9 were present.

(3) The processing method and a possible release of the total material shall be considered as well.

(4) The following indications are intended as guidance for deriving additional protective measures in the course of risk assessment, unless the exonerating criteria according to Section 4.3 para. 3 are fulfilled. The ranking of protective measures must be taken into account.

4.4.1 Substitution

When determining the opportunities for substitution, the hazard characteristics and the release potential under consideration of the physicochemical properties and the conditions of processing and use shall be taken into account as criteria. A substitution analysis shall be carried out considering the TRGS 600 “Substitution”. At present, the following options are considered as suitable for practical implementation:

1. Dust-generating nanomaterials may possibly be dispersed in liquid media, bonded in permanent matrices or replaced by materials generating less dust (through moistening, granulates, pastes or premixed materials).
2. When the nanomaterial is present in a liquid formulation, applications shall be preferred which do not result in aerosol generation.
3. When using fibrous nanomaterials, materials shall be selected which are not biopersistent or rigid or which do not fulfil the WHO fibre criteria.

4.4.2 Technical protective measures

(1) When substitution is not possible, and when there is a higher risk of inhalation exposure, nanomaterials shall be generally manufactured or processed in closed systems or installations as specified in § 9 para. 2 of the Ordinance on Hazardous Substances (GefStoffV). For activities involving small quantities (in the gram or millilitre range) or for nanomaterials showing properties in line with Section 4.3 para. 3, deviations from this principle are possible. When it is technically not feasible to use a closed system, a justification must be given in the documentation of the risk assessment, as it is specified in the TRGS 400 Section 8 para. 1 no. 10.

(2) Existing installations, which are not enclosed, shall be retrofitted with suitable technical protective measures, when this is technically feasible. They include laboratory hoods, for example, as well as safety workbenches, glove boxes, extraction cabinets, object extraction systems or similar, state-of-the-art installations.

(3) In case of necessary activities outside of enclosed systems, i.e. when filling and decanting liquids, an extraction system must be installed at the source. In this context, the requirements for the design of processes performed outside of enclosed systems shall be taken into account in accordance with Section 6.2.2 of the TRGS 500 “Protective Measures”.

(4) When it is not possible to avoid aerosol use, additional protective measures shall be taken. Indications for protective measures for processing varnishes are described in Rule BGR 231 of the German Social Accident Insurance Institution for the building trade (Berufsgenossenschaft der Bauwirtschaft) [20]. In case of an aerosol use involving pure substances or mixtures containing nano-objects, protective measures shall be considered in line with the draft protection guidelines for activities involving biocide products [21].

(5) For activities involving manufactured nanomaterials, which correspond to Section 4.2 para. 2 no. 2 (Biopersistent nanomaterials with specific toxicological properties) and are classified as carcinogenic, as well as nanomaterials corresponding to Section 4.2 para. 2 no. 4 (Biopersistent fibrous nanomaterials), the specifications of

the TRGS 560 “Air re-circulation for activities involving carcinogenic, mutagenic and reproduction toxic particles” shall be taken into account. For plant and equipment such as dust extractors for air re-circulation, the permeability rate of the filter installation or device (and not only of the filter material) must be < 0.005 %. Fixed filter installations shall be monitored for filter breakage and leakage. This may be realised by installing a downstream filter, for example, or by monitoring the residual dust content. The indications in Section 4.4.7 shall be followed for the disposal of filter waste.

(6) To avoid agitating deposits consisting of, or containing nanomaterials, cleaning work must carried out wet or with an industrial vacuum cleaner with an ‘H’ dust class certificate (according to DIN EN 60335-2-69). For cleaning dust-generating nanomaterials with moist or wet methods, powerful water jets should not be used, as they may generate friction and could possibly agitate dust. It is generally not allowed to clean a work area by sweeping it without additional protective measures for binding the dust or by removing dust deposits with pressurised air.

(7) When articles containing nanomaterials undergo abrasive treatments, machines and equipment shall be selected and operated to ensure that as little dust as possible is released. Dust releasing installations, machinery and equipment must be equipped with an effective extraction system, in so far as the state-of-the-art allows and when dust release cannot be prevented by other measures. This principle shall be enforced especially, when articles containing biopersistent fibrous nanomaterials are processed.

(8) When articles containing biopersistent fibrous nanomaterials are abraded and if on the basis of experimental data, a release of such fibres cannot be excluded with any certainty personal protective equipment according to Section 4.4.4 para. 2 no. 3 will possibly be required in addition to technical protective measures.

4.4.3 Organisational protective measures

(1) Employees shall be given targeted instructions on the special physicochemical and toxicological properties of nanomaterials, the potential long-term effects in case of an exposure to nanoscale dusts and the necessity of special protective measures. The working instruction shall be adapted accordingly (see Section 5).

(2) The access to work areas, where activities involving nanomaterials are performed and which are associated with a higher risk, shall be restricted by appropriate actions as specified in § 9 para. 6 of the Ordinance on Hazardous Substances (GefStoffV). For activities involving nanomaterials as described in Section 4.2 para. 2 no. 2 (Biopersistent nanomaterials with specific toxicological properties) and no. 4 (Biopersistent fibrous nanomaterials), it is recommended to mark the entrances to the respective work areas and the workplaces themselves. Only persons which had a course of instruction shall have access to these areas. Work areas, where activities are carried out involving biopersistent fibrous nanomaterials, shall be marked with prohibition sign D-P 006 “No un-authorised access” in line with the Technical Rule for Workplaces (Technische Regel für Arbeitsstätten) ASR A1.3 on “Occupational safety and health signage”.

(3) If the risk potential of nanomaterials has not been subjected to a sufficient toxicological analysis, it must be indicated that the nanoparticle form is a material or substance with partially unknown properties. Such materials shall be labelled in confor-

mity with Section 4.7 of the TRGS 201 “Classification and labelling for activities involving hazardous substances”.

(4) Deposits of nanomaterials shall be avoided.

4.4.4 Personal protective measures

(1) According to § 7 para. 5 of the Ordinance on Hazardous Substances (GefStoffV), the use of burdensome personal protective equipment is not allowed to constitute a permanent solution.

(2) Depending on the outcome of the risk assessment (for example for filter changes of dust removal systems), the following personal protective equipment may be required for activities such as decanting, sampling, as well as cleaning, maintenance and repair work.

1. Body protection: In case of dust generation, a dustproof protective suit with a Type-5 certificate shall be worn.
2. Hand protection: For activities involving nanomaterial powders, chemical protective gloves shall be worn. The limitation to or recommendation of certain types of glove materials is not possible at this time. When nanomaterials are present in liquid form, their resistance to the solvent contained in the liquid shall be considered.
3. Respiratory protection: For activities involving dust-generating nanomaterials, respiratory protection may be required. Both filter and isolation equipment is suitable. The effectiveness of filter devices primarily depends on their tight fit. Half-face respirators with a particle filter (FFP) may offer the desired protection level after checking their tight fit and ensuring their appropriate use. There are advantages in using half-face and full-face respirators with particle filters.

(3) When filter equipment is used for activities involving dust-generating GBP nanomaterials, half-face respirators with a P2 filter or half-face respirators with particle filters of the FFP2 type shall be used up to the current, legally binding limit value for the alveolar dust fraction (3 mg/m^3 at a density of 2.5 g/cm^3). When the occupational limit value is exceeded, half-face respirators with a P3 filter or FFP3-type half-face respirators with particle filters shall be used.

(4) In case of biopersistent nanomaterials with specific toxicological properties and when handling biopersistent fibrous nanomaterials, if filter equipment is used and the values found are not below the detection limit, half-face respirators with a P3 filter or FFP3-type half-face respirators with particle filters shall be used as well, (see also Section 4.5.1 para. 2). The restrictions in accordance with BGR/GUV-R 190 shall be taken into account with respect to the time period for wearing such equipment. For activities requiring a longer time period, it is recommended that half-face or full-face masks with powered TM2P or TM3P particle filters are used.

4.4.5 Unintentional release

(1) In case of an unintentional release, for example a spillage of a larger amount of a dust-generating nanomaterial, unprotected persons must evacuate the work area, if necessary initiate emergency measures and inform employees in adjacent work areas.

(2) The work area may only be entered for cleaning work, when the dust cloud has settled. Even afterwards, a contamination of the air with the nanomaterial must be expected, as nanomaterial behaviour mostly resembles the behaviour of vapours. As a result, with biopersistent nanomaterials a dustproof protective suit with a Type-5 certificate, chemical protection gloves and a tightly fitting respirator with a P3 filter shall be worn in addition to work clothes consisting of work trousers and jacket, safety shoes and eye protection.

(3) The contaminated work area shall be cleaned with liquids and shall only be reopened for further use following a test for its potential contamination.

(4) The spilled nanomaterial, the cleaning agents used and the contaminated protective clothing shall be collected in a tightly closing container and properly disposed of.

4.4.6 Explosion protection against nanoscale dust particles

(1) Flammable bulk solids with a particle size below 500 µm may induce dust explosions and they may form explosive dust/air mixtures, when they are agitated with air. Due to their small particle size, respectively their enlarged surface, nanoparticles, aggregates and agglomerates can be more susceptible to ignition and react more violently than microscale dusts.

(2) When the generation of hazardous explosive atmospheres, for instance by agitating or filling particles cannot be avoided, zones shall be designated in the framework of the risk assessment (see TRGS 720 to 722 or TRBS 2152 and TRBS 2152 Part 1 to Part 4).

(3) Depending on the designation of zones and the probable presence of ignition sources, which are capable of igniting the dust/air mixture, protective measures shall also be taken against explosions.

(4) In order to avoid explosive dust/air mixtures, it is preferable to remove deposits of flammable dust particles with wet cleaning methods or suitable vacuum cleaners.

(5) Examples for avoiding effective ignition sources are the use of equipment (such as fans, vacuum cleaners) with the appropriate equipment certificates according to Directive 94/9 EC and the proper grounding of systems/equipment (see TRBS 2152 Part 3 and TRBS 2153).

4.4.7 Disposal

(1) Nanomaterials shall always be analysed with respect to their chemical composition, classified as hazardous or non-hazardous waste as defined by the waste legislation and treated accordingly. The pre-treatment and packaging of such waste depend on the disposal route and other factors [23].

(2) In addition to such waste-related data, information about the nanomaterial as a waste component and a potential for dust development when opening containers shall be communicated to the specialist disposal company. The disposal shall be discussed and determined in advance with the specialist disposal company or specialist unit.

(3) The hazards and physical properties of waste may be changed by moistening, stabilising or solidifying (by hardening in concrete, for example).

(4) Nanomaterials, which are classified as hazardous and earmarked for disposal, shall be collected in a tightly closing container (such as a PE drum with clamping ring cover), which has been comprehensively labelled in line with legal requirements [23].

(5) With respect to the signage for waste-related activities, we refer to Section 4.6 of the TRGS 201.

4.5 Effectiveness check

(1) The effectiveness of available technical protection measures shall be checked by appropriate investigative methods, which may also include measurements at the workplace.

(2) To determine the specific contamination of employees by manufactured nanomaterials, a standardised measuring method is not available yet.

(3) Because of their low sensitivity, the gravimetric measurements employed as recognised methods for the dust fractions are often not usable for measuring nanomaterials.

4.5.1 Using mass concentrations

(1) If the alveolar fraction of GBP nanomaterials (see IFA Worksheet no. 6068 Alveolar Fraction) does not reach an assessment limit of 0.5 mg/m^3 in conjunction with a density of 2.5 g/cm^3 (see Section 4.2.3 para. 3), the actions set out in §§ 7 and 8 of the Ordinance on Hazardous Substances (GefStoffV) shall suffice. When using a FSP10 sampling head for a period of 2 hours, the detection limit for this method currently is 0.25 mg/m^3.

(2) For nanomaterials with specific toxicological properties, as a minimum the respective occupational limit values and other assessment criteria, which are normally below 0.1 mg/m^3, shall be taken into account. To comply with these very low limits, extensive protective measures are necessary of which effectiveness is high and which have to be employed with consistency. A further differentiation of actions is not

possible at this time. If no occupational limit value (AGW) has been determined yet, for precautionary reasons it is recommended that the determination of their effectiveness shall be orientated to a value of 0.1 mg/m^3. When values are below the detection limit, it may be assumed that actions as defined in §§ 7 and 8 of the Ordinance on Hazardous Substances (GefStoffV) are sufficient.

4.5.2 Using particle number concentrations

(1) It shall be taken into account that there is no generally recognised method yet to determine particle number size distribution. The approach described in this Announcement is intended for stationary workplaces such as those in a production plant. Non-stationary workplaces, which are typical for the construction industry, for example, are not covered.

(2) We propose to use a tiered measuring and assessment method to determine and assess the exposure to GBP nanomaterials, which has been established by various German stakeholders from authorities, the Institute for Occupational Safety and Health of the German Social Accident Insurance, the German Social Accident Insurance for raw materials and chemical industry (Berufsgenossenschaft Rohstoffe und chemische Industrie), science and the Chemical Industry Association (Verband der Chemischen Industrie) [24]. When nanomaterials are present, this method proposes to determine exposure by employing easy-to-use particle-counters such as condensation nucleus counters (CPC) (Level 2: exposure analysis for orientation purposes), and, in a subsequent step, the method proposes to carry out further substance-specific tests (Level 3: detailed exposure analysis).

(3) The assessment of the exposure findings in the context of an analysis for ‚Level 2: exposure analysis for orientation purposes‘ may be performed on the basis of

1. the ubiquitous background contamination with particulate aerosol at the analysed workplace, and
2. a value significantly exceeding this limit,

as long as, or in so far as there are no occupational limit values or suitable health-based proposals for limit values. It is therefore necessary to consider the particle number concentration specifically at the workplace concerned. This should be individually analysed before actually starting the activity. Further guidance for the performance of such measurements may be found in the above-mentioned, tiered approach to determine and assess exposure to nanoscale aerosols.

(4) The decision, whether an exceedance of a limit shall be considered as significant, or whether it represents either a fluctuation of the background contamination with particulate aerosol or an artefact, must be taken by an expert on the basis of the quality of the validation findings. In line with past experiences, it is only safe to assume that the limit value has been significantly exceeded, when the particle concentration increases by a factor of 2 to 3 in relation to the ubiquitous background contamination.

(5) When the particle number concentration for activities involving manufactured GBP nanomaterials shows a significant increase compared to the background concentration of particulate aerosol and when all technical and organisational protective measures have been introduced, more detailed tests (Level 3: detailed exposure

analysis) may be performed using scanning mobility particle sizers and complementary gravimetric sampling in order to arrive at a more clear and possibly exonerating determination of the exposure at the particular workplace compared to the findings of the Level-2 analysis. Gravimetric samples allow a subsequent analysis of the chemical identity of a substance by performing established elemental analyses or using microscopic methods.

(6) For activities involving biopersistent fibrous nanomaterials corresponding to the WHO fibre criteria, and for activities with biopersistent nanofibres, for which morphological tests are not available yet, it would be necessary to determine the fibre concentrations. The objective should be a fibre concentration of less than 10,000 F/m^3 in the workplace air [13]. But validated collection and measuring methods are not available yet. Such methods are currently under development, for example at the Federal Institute for Occupational Safety and Health (Bundesanstalt für Arbeitsschutz und Arbeitsmedizin).

5 Working instruction and information of employees

(1) General specification for the preparation of working instructions and the information of employees are available in the TRGS 555 “Working instruction and information for workers”.

(2) Supplementary information, which is specific for activities involving nanomaterials, has been compiled in this section.

(3) For activities involving mixtures or articles, which contain manufactured nanomaterials and for which a release of such nanomaterials can be excluded, the working instructions in relation to the mixtures or articles are sufficient. If nanomaterials can be released, this has to be mentioned in the working instructions.

5.1 Working instruction for activities involving nanomaterials

(1) Working instructions shall be prepared for specific workplaces and activities. As a consequence, separate working instructions may be required for different activities involving nanomaterials such as cleaning, servicing, maintenance and repair work as well as disposal activities.

(2) When hazardous substances are listed in the working instruction, it shall be indicated that they may be present in nanoscale form.

(3) When describing the hazards for humans and the environment, the hazards caused by particle or aerosol contamination and, if applicable, by dust explosions shall be mentioned specifically.

(4) When describing protective measures and rules of behaviour, the recommendations from Section 4.4 of this Announcement shall be taken into account. In so far as possible, the stated protective measures and rules of behaviour shall be adapted to the specific activity involving the nanomaterial.

(5) When describing the behaviour in emergencies, the recommendations from Section 4.4.5 of this Announcement shall be taken into account. In so far as possible,

the stated behaviour in emergencies shall be adapted to the specific activity involving nanomaterials.

(6) When describing the proper disposal, the recommendations from Section 4.4.7 of this Announcement shall be taken into account.

5.2 Courses of instruction for activities involving nanomaterials

(1) Courses of instruction shall be given specifically for a workplace and an activity. It may therefore be required to target parts of the course of instruction to the requirements for different activities involving nanomaterials such as cleaning, servicing, maintenance and repair work as well as disposal activities.

(2) Beyond the issues discussed in the working instruction as well as those mentioned in Section 5.2 paras. 1 to 3 of the TRGS 555, the course of instruction for activities involving nanomaterials shall also include the following topics:

1. explanation what nanomaterials are,
2. known and suspected safety risks caused by nanomaterials (fire and explosion risks),
3. activities with a higher potential exposure to nanomaterials.

(3) The course of instruction for the employees on the methods and processes, which have to be employed to ensure safety when using nanomaterials, shall include all technical, organisational and personal protective measures, which are determined in the respective working instruction.

(4) Using the risk assessment as a tool, it shall be determined for which methods and processes mentioned in para. 3 additional tutorials or training activities should be carried out. Examples for practical tutorials in using personal protective measures may be:

1. putting on respiratory protection including a check of the correct fit of the respirator and its actual effectiveness,
2. putting on and taking off protective gloves including the correct overlap of the glove and other protective clothing as well as avoiding an exposure of unprotected skin by contaminated gloves,
3. putting on and taking off protective clothing (overalls/protective suits) while avoiding an exposure of the skin or clothing by contaminated protective clothing.

(5) For the tutorials and training activities to be performed in accordance with para. 4, the employer shall determine the criteria for monitoring both their success and their frequency.

5.3 Occupational-medical and toxicological advice for activities involving nanomaterials

Beyond the issues mentioned in Section 5.2 paras. 4 to 9 of the TRGS 555, the following topics should also be taken into account for the occupational-medical and toxicological advice on activities involving nanomaterials:

1. known and suspected health risks (properties hazardous to health) of nanomaterials, and
2. uptake routes of nanomaterials into the body.

6 Documentation

(1) Specifications for the documentation of risk assessments are available in Section 8 of the TRGS 400.

(2) For activities involving nanomaterials, which are classified as carcinogenic, mutagenic or reproduction toxic, Categories 1 or 2, § 14 para. 3 nos. 3 and 4 of the Ordinance on Hazardous Substances (GefStoffV) shall be taken into account.

Literature

[1] Commission Recommendation of 18 October 2011 on the definition of nanomaterial (2011/696/EU), Official Journal of the European Union L 275/38 of 20 October 2011 http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CELEX:32011H0696:EN:NOT

[2] Ausschuss für Gefahrstoffe (AGS), Wissensstand bezüglich möglicher Wirkprinzipien und Gesundheitsgefahren durch Exposition mit arbeitsplatzrelevanten Nanomaterialien [Current intelligence regarding potential modes of action and health hazards caused by exposure to workplace-related nanomaterial] (Status as of 24 March 2011) http://www.baua.de/de/Themen-von-A-Z/Gefahrstoffe/AGS/AGS-zu-Nanomaterialien.html

[3] DIN ISO/TS 80004-1, Nanotechnologies - Vocabulary - Part 1: Core terms

[4] Begriffsglossar zu den Regelwerken der Betriebsicherheitsverordnung, der Biostoffverordnung und der Gefahrstoffverordnung [Glossary of terms on the rules of the German Ordinance on Industrial Safety, the Biological agents Ordinance and the Ordinance on Hazardous Substances] (Download of 20 March 2013) http://www.baua.de/de/Themen-von-A-Z/Gefahrstoffe/Glossar/Glossar.html

[5] European Chemicals Agency (ECHA), Guidance on the compilation of safety data Sheets, Version 1.1, December 2011 (Download of 20 March 2013) http://echa.europa.eu/documents/10162/13643/sds_en.pdf

[6] Verband der chemischen Industrie (Chemical Industry Association, VCI), Produktverantwortung bei Nanomaterialien [Product responsibility regarding nanomaterial] (Download of 20 March 2013) https://www.vci.de/Themen/Chemikaliensicherheit/Nanomaterialien/Seiten/Nanomaterialien---Position-des-VCI-zur-Produktverantwortung.aspx#

[7] Berufsgenossenschaft der Bauwirtschaft (German Social Accident Insurance Institution for the building trade), Nanoteilchen in Bau- und Reinigungsprodukten [Nanoparticles in building and cleaning products] (Download of 20 March 2013) http://www.bgbau.de/praev/fachinformationen/gefahrstoffe/nano

[8] European Chemicals Agency (ECHA), Registered substances (Download of 20 March 2013) http://apps.echa.europa.eu/registered/registered-sub.aspx

[9] BAuA-VCI, Empfehlung für die Gefährdungsbeurteilung bei Tätigkeiten mit Nanomaterialien am Arbeitsplatz [Guidance for the risk assessment of activities involving nanomaterial at the workplace], May 2012 (Download of 20 March 2013) http://www.baua.de/de/Publikationen/Fachbeitraege/Gd4.pdf?__blob=publicationFile&v=3

[10] Untersuchungen der Lackindustrie zur Freisetzung von Nanopartikeln aus Lackoberflächen [Studies of the varnish industry on the release of nanoparticles from varnished surfaces] (Download of 20 March 2013) http://www.lacke-und-farben.de/magazin/wissenschaft-technik/untersuchungen-der-lackindustrie-zur-freisetzung-von-nanopartikeln/

[11] Leitfaden zum Umgang mit Nanoobjekten am Arbeitsplatz [Guideline for handling nano-objects at work]; Verband der deutschen Lack und Druckfarbenindustrie e.V. (Association of the German Varnish and Printing Inks Industry, VdL) (Download of 20 March 2013) http://www.lackindustrie.de/Publikation/Technische-Veroeffentlichungen/Seiten/Technische-Veroeffentlichungen.aspx

[12] Announcement on Hazardous Substances 409 „Nutzung der REACH Informationen für den Arbeitsschutz“ [Using REACH information for health and safety at work] http://www.baua.de/en/Topics-from-A-to-Z/Hazardous-Substances/TRGS/Announcement-409.html

[13] Institut für Arbeitsschutz der DGUV (Institute for Occupational Safety and Health of the German Social Accident Insurance), Maßstäbe zur Beurteilung der Wirksamkeit von Schutzmaßnahmen [Criteria for assessing the effectiveness of protective measures] (Download of 20 March 2013) http://www.dguv.de/ifa/Fachinfos/Nanopartikel-am-Arbeitsplatz/Beurteilung-von-Schutzma%C3%9Fnahmen/index-2.jsp

[14] IG Bergbau, Chemie, Energie, (Mining, Chemical, Energy Industry Workers‘ Union) Nanomaterialien – Herausforderung für den Arbeits- und Gesundheitsschutz [Nanomaterial – a challenge for occupational health & safety] (Download of 20 March 2013) http://www.igbce.de/download/15052/2/nanomaterialien.pdf

[15] European Pharmacopoeia, 7th Edition, Amtliche Deutsche Ausgabe (Official German Edition), ISBN 978-3-7692-5909-4, 2011

[16] Informationen zum OECD-Testprogramm [Information on the OECD test programme) (Download of 20 March 2013) http://www.oecd.org/env/ehs/nanosafety/sponsorshipprogrammeforthetestingofmanufacturednanomaterial.htm

[17] BAuA, Gesundheitliche Wirkung von partikulären Nanomaterialien – derzeitiger Kenntnisstand [Health effects of particulatenanomaterial – current intelligence] (Download of 20 March 2013) http://www.baua.de/de/Themen-von-A-Z/Gefahrstoffe/Nanotechnologie/pdf/Vortrag-Gebel-01.pdf?__blob=publicationFile&v=2

[18] Gebel, T. Small difference in carcinogenic potency between GBP nanomaterial and GBP micromaterials. Arch Toxicol (2012) 86:995-1007

[19] DGUV Sachgebiet AK Laboratorien der DGUV (DGUV Desk Laboratories Working Party of DGUV): Nanomaterialien im Labor Hilfestellung für den Umgang [Nanomaterial in the laboratory, guidance for their handling] (Download of 20 March 2013) http://www.bgrci.de/fileadmin/BGRCI/Downloads/DL_Praevention/Fachwissen/Laboratorien/Nanomaterialien_im_Labor20120305.pdf

[20] Berufsgenossenschaft der Bauwirtschaft (German Social Accident Insurance Institution for the building trade), BGR 231, Schutzmaßnahmenkonzept für Spritzlackierarbeiten – Lackaerosole [Concept of the protective measures for varnish spraying - varnish aerosols] (Download of 20 March 2013) http://www.bgbau-medien.de/html/pdf/bgr/bgr_231.pdf

[21] Entwürfe der Schutzleitfäden für Tätigkeiten mit Biozidprodukten Sprühen von Holzschutzmitteln [Drafts of the protective guidance documents for activities involving biocidal products - Spraying wood preservatives] (Download of 20 March 2013) http://www.baua.de/de/Forschung/Forschungsprojekte/pdf/Holzschutzmittel-4.pdf?__blob=publicationFile&v=1

Sprühen von Insektiziden [Spraying insecticides] (Download of 20 March 2013) http://www.baua.de/de/Forschung/Forschungsprojekte/pdf/Insektizide-5.pdf?__blob=publicationFile&v=1

[22] Hinweise zu staubarmen Bearbeitungssystemen [Guidance on low-dust processing systems] (Download of 07 May 2013) http://www.bgbau.de/gisbau/fachthemen/staub/staubarme-bearbeitungssysteme/staub_bea.htm

[23] Verband der chemischen Industrie e.V. (Chemical Industry Association, VCI), Leitfaden: Sichere Entsorgung von Abfällen, die Nanomaterialien enthalten [Guidance: The Safe disposal of wastes containing nanomaterial] (Download of 20 March 2013) https://www.vci.de/Services/Leitfaeden/Seiten/Sichere-Entsorgung-von-nanohaltigen-Abfaellen.aspx

[24] BAuA, BG RCI, IFA, IUTA, TUD, VCI: Tiered Approach to an Exposure Measurement and Assessment of Nanoscale Aerosols Released from Engineered Nanomaterial in Workplace Operations, 2011 (Download of 20 March 2013) https://www.vci.de/Downloads/Tiered-Approach.pdf

[25] National Institute of Occupational Safety and Health (NIOSH), NIOSH Current Intelligence Bulletin 63: Occupational Exposure to Titanium Dioxide, April 2011(Download of 20 March 2013) http://www.cdc.gov/niosh/docs/2011-160/pdfs/2011-160.pdf

[26] National Institute of Occupational Safety and Health (NIOSH), Draft NIOSH Current Intelligence Bulletin: Occupational exposure to carbon nanotubes and nanofibers, December 2010 (Download of 07 May 2013) http://www.cdc.gov/niosh/docket/archive/pdfs/NIOSH-161-A/0161-A-110110-DraftDocument.pdf

Appendix 1
Specimen letter to manufacturers

Dear Madam, Dear Sir (manufacturer/distributor),

We currently use the product (exact name) manufactured/distributed by your company. We have reason to assume that it is a manufactured nanomaterial according to the recommendation of the European Commission on the definition of nanomaterial or that such nanomaterial is contained therein. In the course of our information gathering for a risk assessment pursuant to the TRGS 400, we would ask you to provide additional data on your product. Please send us information on the following points (when available):

1. classification of the nanoscale form
2. particle number size distribution
3. specific surface
4. morphological information (form and structure, especially in case of fibres and with regard to the applicability of the WHO fibre criteria, for example)
5. surface modification of the nano-objects
6. solubility in water
7. data on the product‘s dustiness
8. flammability data (flammability and explosion limits, for example)

Yours sincerely

Appendix 2
Published recommendations for assessment criteria

Legally binding, health-based occupational limit values for manufactured nanomaterials are currently not available. The following recommendations of various organisations or manufacturers may be used as reference assessment criteria following an appropriate assessment by an expert. (Status as of 20 March 2013).

Publisher	Nanomaterial	Recommended limit value	Source
Institute for Occupational Safety and Health of the German Social Accident Insurance	biopersistent granular nanomaterial density > 6000 kg/m^3	20 000 particles/cm^3 in the measurement range from 1 to 100 nm	[13]
Institute for Occupational Safety and Health of the German Social Accident Insurance	biopersistent granular nanomaterial density < 6000 kg/m^3	40 000 particles/cm^3 in the measurement range from 1 to 100 nm	[13]
Institute for Occupational Safety and Health of the German Social Accident Insurance	carbon nanotubes (CNT), where the WHO fibre characteristics cannot be excluded	10 000 fibres/m^3	[13]
National Institute of Occupational Safety and Health (NIOSH)	titanium dioxide (< 100 nm),	0.3 mg/m^3, 10 h/day and 40h/week,	[25]
National Institute of Occupational Safety and Health (NIOSH)	carbon nanotubes and -fibers	0.007 mg/m^3 (measured as elementary carbon)	[26]
Manufacturer	Multi-walled carbon nanotubes (MWNTs)	0.05 mg/m^3	[8]

Appendix 3
Flowchart with a simplified description of the procedure to be followed in the risk assessment of nanomaterials