The production of nanomaterials is booming worldwide. At the same time, they are suspected of having serious health effects.
Nanomaterials: Why risk assessment is so difficult

Any nanomaterial is equal to one billionth of a metre. In contrast to traditional industrial manufacturing processes, which produce ultra-fine particles with a size of 10 to 5,000 nm, nanomaterials contain particles with a size of just 1 to 100 nm. The fineness of the particles, their use in great numbers and the tendency to change their formation and their external appearance by forming agglomerates allow nanomaterials to form extremely large surfaces. Their physical/chemical properties are highly reactive—much higher than their original substances. This means that they can be used to manufacture products in a more compact form than was previously possible; they can help to significantly reduce the product weight or improve the product properties of durability, contamination resistance, solubility and conductivity.

However, the benefits of nanomaterials must be weighed against their disadvantages: It is considered likely that if inhaled, consumed orally or if they come into contact with the skin, nanomaterials can penetrate deep into the bodies of living organisms and have a carcinogenic or even a genetically harmful effect.

What are Nanomaterials?
Nanomaterials are rapidly increasing in importance around the world. The open US database project PEN—the Project on Emerging Nanotechnologies currently lists over 1,800 products that contain nanomaterials. In particular, they are used to manufacture cosmetics, batteries, textiles, paints and coatings as well as food. Nanomaterials refer to substances that contain nano-objects—in individual form, or loosely or firmly connected to each other as agglomerates. Nano-objects include nanoparticles, nanorods and nanoplatelets. They are measured in nanometres (nm); 1 nm is equal to one billionth of a metre.
Nomenclature of nanomaterials according to ISO TS27687

Source:
Institute of Energy and Environmental Technology (IUTA), Duisburg; Center for Nanointegration Duisburg-Essen (CeNIDE), Duisburg; https://www.aerztekammer-bw.de/10aerzte/20fortbildung/20praxis/85arbeitsmedizin/1112.pdf
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as describing the potential exposure types (inhalation, skin contact, ingestion) and deciding the sampling and measurement methods to be used to document the exposure.

In general, the OSHA (US) recommends only working with nanomaterials in closed rooms or under an exhaust hood. Dry sweeping or the swirling up of dusts must also be avoided. In addition, employees should be equipped with adequate personal protective equipment, such as respiratory protection devices, gloves and protective clothing. But what does adequate mean in relation to nanomaterials?

Many countries with industries that use nanomaterials generally ensure that employees are entitled to protection against workplace impairments. Some industrialised nations have even taken it a step further. In such cases, specific occupational health and safety recommendations for handling nanomaterials have been provided. Directive 89/391/EEC from the European Agency for Safety and Health at Work, for example, states that employers must regularly carry out workplace-related risk assessments and take adequate prevention measures. This also explicitly relates to potential risks resulting from the use of nanomaterials. Even stricter provisions apply if nanomaterials have already been identified as hazardous substances, e.g. included in databases such as the Registration, Evaluation and Authorisation of Chemicals (REACH) or the Classification, Labelling and Packaging (CLP) database, or if their carcinogenic or genetically harmful effect has been demonstrated. In 2012, the European Union (EU) also established the ‘Nano-device’ project, which also aims to develop standards regarding personal protective equipment (PPE), including respiratory protection, hand and arm protection and life jackets—results not yet published.

The U.S. agency Occupational Safety & Health Administration (OSHA) has already published corresponding regulations on working with nanomaterials. It recommends identifying the typical processes and procedures during which employees may be exposed to nanomaterials. This includes determining the physical state of the material (dust, powder, solid or liquid aerosols) as well as describing the potential exposure types (inhalation, skin contact, ingestion) and deciding the sampling and measurement methods to be used to document the exposure.

The devil is in the detail, i.e. in the risk assessment of workplaces that may potentially be contaminated by nanomaterials. First of all, a reliable risk assessment is only possible if you are aware that nanomaterials could be present and know which they are. The toxicity evaluation is another difficulty in substance identification, as the selection of appropriate protective equipment depends on the toxicity of the substances that may potentially be present. Official occupational exposure limits recognised by national or international

Guideline for industrial health and safety when working with nanomaterials

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In summary, it can be stated that it is currently impossible to determine the toxicity of nanomaterials as a whole. It depends on the manufacturing process, the size of the surface and its state. However, in view of the current state of flux in terms of knowledge and technology, it is not possible to rule out that further criteria may become necessary to determine toxicity.

1. How can the toxicity of nanomaterials be identified?

The toxicity of substances has previously always been defined as a proportion to mass (e.g. ppm—parts per million as a measure of concentration). This seemingly no longer applies for nanoparticles. In this case, the surface area is more important. As extremely large numbers of nanoparticles are present on a support material, their total surface area is also very large.

Determining the toxicity of these substances is a major problem. Titanium dioxide (TiO$_2$), for example, is a nanomaterial that is used quite frequently in skin creams as well as in façade paints. But it is not possible to determine the toxicity of 10 nm of titanium dioxide, as it depends on how the substance was produced. The substance displays different toxicities depending on whether chemical process X or chemical process Y was used. Viewed externally, the material is essentially the same, but various substances that may cause different chemical reactions may be present on the surface. In practice, it is extremely difficult to achieve a specific surface in a controlled manner when manufacturing nanomaterials. This is also due to the fact that nanoparticles tend to agglomerate.

In the case of liquid aerosols, e.g. in the painting industry, the particles become smaller over time and the solvent evaporates. If an organic solvent is used, a gas filter should be used in addition to the particle filter for protection against organic vapours, as there is the risk of inhalation both in liquid and in gaseous state. “There is evidence to suggest that, because nanoparticles have continued to decrease in size over the past few years as technology has advanced, these particles can be inhaled into the alveoli, pass through the blood barriers and even reach the brain. This is not possible for larger particles”, says Dr Harald Heyer, Research & Development Chemical Components, Dräger Safety AG & Co. KGaA, Lübeck/Germany.

2. Why is it so difficult to clearly characterise nanomaterials?

A major difficulty in characterising nanomaterials is that small particles tend to form agglomerates. These agglomerates may be incorrectly identified as a single larger particle during measurement. However, if it is an agglomerate and not actually a large particle, this may subsequently be destroyed during processing or as a result of other physical reactions. In turn, this once again releases a multitude of small particles. As a result, it is possible that the potentially hazardous character of the material is not detected during measurement.
Nanomaterials: Why risk assessment is so difficult

50 and 100 nm. While SMPS (scanning mobility particle sizers) are available and can measure particles larger than 2 nm based on the principle of particle movement in an electric field, these measuring instruments are extremely expensive, are sometimes equipped with radioactive sources and are not mobile. Moreover, aerosols that contain nanoparticles can be extremely volatile, i.e. do not continue to exist as such for a long period of time. The large agglomerated particles settle and the small ones evaporate. As a result, taking samples at the production plant to be sent to a remote SMPS location does not make much sense. If an air sample is taken, the particles may settle on the wall of the sample container, which means that they can no longer be measured as freely moving particles.

Employers currently need to apply several measurement methods, compare the results and perform a risk assessment on this basis.

Initial international and national approaches are attempting to define occupational exposure limits. However, the definition of occupational exposure limits requires the identification of the existing substances and their toxicity. The difficulties involved in this process are explained under Point 2. As a result, this process is still in its infancy. However, initial guidelines are already available. For example, the US National Institute for Occupational Safety and Health (NIOSH) recommends an exposure limit (REL—recommended exposure limit) of 2.4 mg/m$^3$ for the titanium dioxide pigment (TiO$_2$) and 0.3 mg/m$^3$ for ultra-fine titanium dioxide. NIOSH classifies the latter as a potential carcinogenic substance. NIOSH has also developed a comprehensive guide for occupational exposure to the potentially carcinogenic substance CNT (carbon nanotubes). It is recommended that maximum exposure to respirable CNT should not exceed a value of 1.0 µg/m$^3$ per TWA (time-weighted average).

Optical measuring systems can generally be used for aerosols. However, the measuring limit for conventional systems lies between 3. How can the number and size of nanoparticles even be measured

The number and size of nanoparticles are still often determined using mass measurement methods or particle counters. However, these methods cannot distinguish between agglomerates and individual particles. Measurement is made more difficult in that small particles can float in the air for a long period of time and have a very low mass. This means that the scope of the risks cannot be specified and limited, unless the work is performed in a closed system with exhaust ventilation. These days, personal samplers are generally used in the chemicals industry. These units collect particles separated in the manufacturing area as samples. They are then evaluated by being counted under an electron microscope. This allows you to identify the geometric size, but it does not necessarily allow you to draw conclusions about the selection of adequate occupational health and safety measures. According to Dr Heyer: “The measurement of the aerodynamic diameter would provide the most information. It determines what parts of the body the particle can reach after inhalation—whether it is caught in the lungs or whether it can penetrate into the alveoli. The problem is that most measuring instruments are based on the principle of light scattering and do not provide information on the aerodynamic diameter.”

4. Why is it so difficult to measure aerosols that contain nanoparticles?

5. How can an employer perform a risk assessment in these circumstances?

Employers currently need to apply several measurement methods, compare the results and perform a risk assessment on this basis.

6. What about the binding definition of occupational exposure limits?

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A current recommendation for working with nanomaterials is to use a full face mask or half mask with a class P2 or P3 filter, i.e. a filter with a filter performance of at least 94% (P2) or 99.95% (P3). In contrast to what is often assumed by laypeople, this kind of depth filter does not act like a sieve: A sieve collects the large parts, while the small parts slip through. By contrast, a depth filter retains the small nanoparticles just as well as large ones. It is the medium-sized nanoparticles that tend to cause a problem. They are the ones that are most likely to slip through the filter. Findings suggest that the minimum filtration efficiency, i.e. the point at which most particles can penetrate through the filter, for electrostatic filters is for particle sizes of about 40 nm. For mechanical filters, the minimum filtration efficiency occurs for particles with a size of about 150 nm. A choice generally has to be made between mechanical and electrostatic filters. The latter are based on the principle of substance bonding using an electrostatic charge. This charge can be disturbed by aerosols as well as incorrect storage conditions (temperature, humidity) which results in a reduction of the filter performance. These electrostatic filters are less expensive but, as mentioned above, are also more vulnerable and their protection is not as effective.

For liquid aerosols, the drops that are separated are liquid, while the drops are solid for solid aerosols. These aerosols have a different effect on the filter materials. If solid aerosols are separated in the filter, the
breathing resistance tends to increase rapidly. However, for liquid aerosols, a much higher volume has to be separated before this negative effect becomes noticeable. In principle, it is recommended that users replace the filter as soon as they notice a rise in breathing resistance.

9. What other critical factors need to be considered when selecting respiratory protection for nano-aerosols?

Attention must also be paid to mask leaks, i.e. the seal to the face. This is much greater for a particle-filtering half mask than for a reusable polymer-based or silicon mask. One option would be to select a high-quality reusable mask instead of a disposable particle-filtering face piece, even if this happens to be a very good one.

10. What other general criteria need to be noted?

“The selection of the filter system always depends on the local situation. If the user only comes into contact with particles, then a particle filter should be the first choice. However, if gases are also present, due to the evaporation of the particles, a combination filter needs to be used”, according to Dr Heyer. The user’s wearing comfort also plays a role:

Electrostatic materials generally have much lower breathing resistances than conventional materials. However, as mentioned above, there is also the drawback that they may be damaged by aerosols and storage conditions and have a shorter service life. “This means that a general recommendation on filter selection is impossible”, says the Dräger expert.

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