

Fact Sheet

Use of nanomaterials in coatings

1. Description of application

1.1 Products and purpose of using nanomaterials¹

Automobiles, planes, ships, machinery, facades and the interior of buildings, furniture, household appliances, magazines, posters and data storage devices: The list of products covered with lacquers and paints is sheer endless. In 2012 about 2.6 million tons of lacquer, paint and printing ink were produced in Germany (VdL 2013). This shows how important these products are in our daily lives. Surfaces are coated with lacquer or paint to protect them against mechanical, chemical and weather-related impacts but also to improve their aesthetic appearance. To meet the ever-growing demands on modern coatings, the paint industry continuously strives to improve their products. Therefore, over the past years nanotechnology has become more and more important in the development of coatings. The German Paint and Printing Ink Industry Association (VdL) assumes that within the next 10 years in Germany about 20 % of the turnover of the branch will come from the use of nanotechnology, in the form of so-called „smart coatings²“ (VdL 2010).

Additives containing nanoscale materials have long been used in the production of lacquers and paints, for example, barium sulphate and iron oxide as colouring pigments and synthetic amorphous silica to influence the fluidity of lacquer. In recent years modern techniques have been developed to visualize and scientifically describe nano-scale materials and structures. It is therefore now possible to tailor the manufacture and use of nanomaterials and nanostructures in the coating industry to the specific needs of the various applications. Novel nano-based coatings are widely used today, for instance, to functionalize surfaces, to provide protection

¹ Nanomaterials consist of definable structural components with a size range of 1 - 100 nanometres (1 nm = 10⁻⁹ m) in at least one dimension (See also the Commission's recommendation of 18 Oct 2011 for the definition of nanomaterials (2011/696/EU)). Nanoparticles are a subset of nanomaterials having the above size range in all three dimensions. Both natural and anthropogenic nanomaterials occur in the environment. Nanotechnology uses engineered nanomaterials.

² “Smart coatings” are coatings with additional functions like thermal insulation, self-cleaning properties, controlled release of active ingredients or self-healing functions.

against corrosion and dirt, to prevent biological soiling³ and graffiti or to create attractive designs by special colour effects (Luther and Zweck 2006).

1.2 Nanomaterials contained in coatings

What is a „coating“?

A coating is defined as a coherent layer formed from a single or multiple application of a coating material to a substrate (DIN EN ISO 4618; 2.52)⁴. According to the existing standard (DIN EN ISO 4618; 2.53) a coating material is a material in liquid, paste or powder form which, when applied, forms a protective and decorative coating. Coating materials are complex chemical products; the term "coating materials" includes "lacquers", "paints" and similar products. In most cases coatings consist of the following four types of ingredients:

- ▶ **Binders (also called "film formers")**
In most cases binders are based on organic polymers or intermediate products. They ensure that during the drying and hardening of the lacquer a coherent film is formed.
- ▶ **Pigments and extenders**
In most cases pigments are insoluble colour particles. They are used as colourant.
Extenders are used to create or modify certain physical properties. Most of the extenders are naturally occurring mineral fillers and insoluble in solvents and binders.
- ▶ **Solvents**
Solvents are single liquids or blends of liquids that dissolve other substances to form solutions without reacting with these substances (except reactive solvents). Conventional types of lacquer contain organic solvents like esters, glycol ethers or aliphatic hydrocarbons.
Organic solvents are more and more replaced by water. Water-based paints contain other binders; Also, in most cases the binder is not dissolved but dispersed ("dispersion lacquers").
- ▶ **Additives**
In terms of their chemical composition, additives are very diverse. Usually they are added to a coating material in very small quantities only. In the coating material they can modify a large variety of properties, for instance, its flow behaviour, surface tension, gloss, structure, UV and weather resistance.

The mass fraction of a nanomaterial in a coating system depends on the desired function. For example, when adding nanomaterials to a lacquer to improve its wear resistance, their mass fraction amounts to 3 - 7 % (Deutsches Lackinstitut 2011). Depending on the desired function, nanotechnology-based functional coatings typically contain the following nanomaterials: Titanium dioxide, silicon dioxide, carbon black, iron oxide, zinc oxide and silver. Table 1 contains a number of other nanomaterials that may be added.

In practice, there is always more than one particle size present. Particle size distribution typically extends over at least one order of magnitude. Before they are processed, the particle size of pigments ranges from several tens to several thousand nanometres⁵. Binders that can be dispersed in water using a stabilizer form small particles with diameters in the range

³ In Germany structural damage caused by biological soiling of facades is estimated to be in the order of magnitude of 2 to 4 billion € per year.

⁴ DIN EN ISO 4618 Standard „Paints and varnishes – Terms and definitions“ (ISO/DIS 4618:2013)

⁵ The colour intensity of pigments is mainly determined by particle size. The smaller the particles the richer the colour. Growing particle size also changes the shade of the colour.

of 50 to approximately 500 nm. While the coating is drying the particles merge. For applications that require certain technical properties (e.g. scratch resistance) particles with a narrow particle size distribution (monodispersity) are preferred. *The term "nanomaterials" used herein refers to this type of materials.*

Table 1

Selected applications of nanomaterials in coatings and their functions (according to Paschen et al. 2003, Deutsches Lackinstitut 2012, BG BAU 2013)

Function	Nanomaterial (Examples)	Advantage/Effect	Industrial Branch
Colour brilliance, shade, colour effects (flip-flop effect), reproducible paints, easily dispersible paints	Carbon black; Oxides (TiO ₂ , Fe ₂ O ₃ , Fe ₃ O ₄ , SiO ₂ , Cr ₂ O ₃) (on mica flakes or SiO ₂ spheres, with metal pigments), ZnO	Intensify effects of metal pigments; Stabilize pigments and fillers; Positive effects in dispersion paints; Prevent crack formation (Phyllosilicates/sheet silicates); Improve resistance to fading	Automotive, consumer goods (furniture), construction
Self-cleaning („easy-to-clean“)	Organic-inorganic hybrid polymers (organically modified ceramics), nanosilica/colloidal silica embedded in resin particles following polymerisation; Silanes (silicon-based mixtures with other chemicals, e.g. fluorine compounds); TiO ₂	Dirt and water repellant, Protection against algae and fungi; Anti-graffiti protection: Easy removal of unwanted paint	Automotive, construction (facades), glass
Switchable (electrochromic, photochromic, thermochromic)	Tungsten oxide (WO ₃) (electrochromic)	Colour effects	Automotive
„Self-Assembly“	Polymer gel, specific organic-inorganic hybrid polymers	Self-healing surfaces	Automotive, cosmetics
Monolayer adhesive films	Polymers	Ultra-thin layers	Automotive, consumer goods
Scratch resistance	Oxide (synthetic amorphous silica), SiO ₂ , Al ₂ O ₃)	Improved scratch resistance	Automotive, information and communication, parquet flooring, consumer goods (furniture), optics (lenses)

Function	Nanomaterial (Examples)	Advantage/Effect	Industrial Branch
Optimized flow characteristics	Oxide (synthetic amorphous silica)	Generate new rheological properties (elasticity, flow characteristics, thixotropy)	Various
Conductive coatings for electrostatic paint spraying	Carbon: Fullerenes, carbon nanotubes (CNT)	Enhanced spraying processes	Automotive
Photocatalytic effect, antimicrobial effect	TiO ₂ , ZnO ⁶ , Ag	Removal of grease, dirt, algae, bacteria, fungi, odourants and pollutants, transformation of NO _x and ozone from the atmosphere into harmless compounds.	Construction (facades, noise barriers, tiles), road surface, vehicles, wood preservation, glass
Fire retardant	SiO ₂	When a certain temperature is exceeded, a heat-insulating carbon foam layer is created on the wood surface followed by a flame-resistant ceramic layer.	Construction, protection of wood against fire
Corrosion protection, wood preservation	Zinc or aluminium coated with nano-TiO ₂ , nanoclay (like hydrotalcite Mg ₄ Al ₂ (OH) ₁₂ CO ₃ xH ₂ O)	Nanoclay coatings delay the fading of wood (which is a result of the bleeding of complex chemicals like tannins).	Construction, automotive, wood preservation
UV protection, IR reflective or IR absorbing	(TiO ₂ ; ZnO, CeO ₂ , iron oxide pigments (transparent iron oxide; needle-shaped particles with a length of 50-100 nm and width of 2 nm)	Enhanced UV resistance, blocking of IR and visible light, indoor climate control	Construction (facades), wood preservation, glass, plastics

Nanomaterials are used to achieve higher opacity, better interaction between coating and surface and higher durability of the coating. Due to their small particle size of 100 nm or less, some nanomaterials are suitable for use in transparent coating systems. In addition, the transparency of these nanomaterials (e.g. of TiO₂ in visible light) makes it possible to create novel additives introducing new properties to otherwise non-transparent coatings.

⁶ The above source mentions the antimicrobial effect of zinc oxide in lacquer. It should, however, be noted that this substance is neither listed as biocide in the list of permitted active substances ("Biozid-Wirkstoffverfahren") nor in any of the annexes to the new Biocides Regulation. It is therefore not allowed to use this substance for this purpose or to advertise it as having an antimicrobial effect in lacquer.

Depending on their structure, nano-based coatings very often fall under the definition of "nanocomposite" or "nanohybrid" materials. A nanocomposite/nanohybrid is a combination of several materials. Its material properties differ from the ones of its individual components. Thus it is possible, for instance, to combine contradictory properties like hardness and elasticity instead of hardness and brittleness.

Nanomaterial-containing coatings offer much better material and processing properties than conventional coatings (e.g. increased indentation resistance, high elasticity, fast drying, no expansion after contact with water, high water vapour permeability). These properties are used, for example, to produce nanocomposite-based wood stain that cures faster (early blocking resistance) and has a higher elasticity (Leuninger et al. 2004).

Photocatalytical TiO₂-coatings offer self-cleaning properties as well as an antimicrobial effect. As these surfaces are also highly water-repellant, they are suitable, for example, for the following applications: Mirrors, self-cleaning windows, window frames, bricks, wall paint, tiles, flat glass.

Nanomaterial additives in coatings are expected to replace halogenated flame retardants, which are hazardous to the environment. Nanocoatings are applied directly to the surface to be protected (glass, wood, metal, plastics or concrete). In the event of a fire, a ceramic layer is formed within seconds. It provides insulation against heat and drastically reduces the amount of smoke generated (Luther and Zweck 2006). Carbon nanotubes (CNT) play a growing role in discussions of fire-retardant coatings (Rössler 2007).

Other applications of specialty coatings include products that have to meet strict requirements regarding transmittance and antireflection, e.g., glass covers for photovoltaic modules and solar water heaters or certain architectural and greenhouse applications. Anti-reflective coatings can increase the energy transmittance of glass by 6% (Hofmann 2006). Nanomaterial-containing coatings used on steel surfaces are expected to improve corrosion protection and replace chromate, which is hazardous to the environment (Goedicke 2009).

1.3 Manufacture

Just like conventional systems, nano-based coatings have to meet many different requirements and pass all necessary field tests before they are applied in practice.

Depending on their future use, nanocoatings require a clearly defined and narrow particle size distribution (monodispersity). By using certain synthesis processes it is possible to generate nanomaterials that are tailored

to specific applications. In principle, there are two approaches to nanostructures: A "top-down" approach and a "bottom-up"⁷ approach. Described below is only a selection of relevant production techniques. Due to the great variety of possible applications and application-specific manufacturing processes it is not possible to describe all available techniques in the present document.

The so-called sol-gel process plays an important role in the production of nano-based coatings. During this process, a sol (i.e. a viscous colloidal solution) is applied to a surface by means of conventional coating processes (e.g. dip, spray or spin coating). The thickness of the layers that are generated ranges between 0.5 and 3 µm. In extreme cases they may be just a few nanometres thick and be transparent. Increased durability of the coating can be achieved by burning the coating at high temperatures onto the surface. Another example: When a porous SiO₂ layer is applied onto a glass surface and subsequently hardened at high temperatures, an anti-reflective behaviour over a very broad spectral range can be achieved due to the porosity of this SiO₂ single-layer system.

Sols that dry at room temperature to form a solid coat are available on the market in quite a number of (liquid or spray) products. They can be used by the consumer on finished products (e.g. windows, tiles etc.). However, these coatings are not durable (Greßler et al. 2010).

The use of nano-based coatings on exterior facades is based on the use of inorganic/organic nanocomposites as binders in water-based facade coatings. Nanocomposites are prepared by emulsion polymerization of acrylates in silica sols. By using this technique, it is possible to achieve a homogeneous distribution of silica nanoparticles in the polymer and a silica content of up to 50 % in the nanocomposites. The inorganic ingredients significantly improve the scratch resistance and hardness of the coating. In addition, the surface obtains superhydrophilic properties due to the high concentrations of polar silanol groups. These properties generate a self-cleaning effect on the facade (Luther and Zweck 2006).

Photocatalytic coatings with nanoscale TiO₂ are typically applied via chemical vapour deposition (CVD)⁸. This type of coating is not only used on glass surfaces but also on plastics (PVC), acoustic panels, ceramic tiles, roof tiles and concrete slabs. The choice of the manufacturing process depends on the specific application and the specific application require-

⁷ Top-Down: Nanostructures are generated by mechanical disintegration (milling) of the original material;

Bottom-Up: Nanostructures are built up in a chemical process.

⁸ During chemical vapour deposition a solid material from the gaseous phase is deposited onto the surface of the substrate as a result of a chemical reaction. This coating technique allows the application of a homogeneous coat inside very small depressions or onto the inner surface of a hollow body.

ments of the coating. The sol-gel process may offer several advantages to manufacturers: The manufacturing process is shorter, runs at lower temperatures and consumes less energy.

1.4 The release of nanomaterials

The possible release of nanomaterials from coatings has already been subject of various studies (Vorbau et al. 2009, Guiot et al. 2009, Göhler et al. 2010, Göhler et al. 2013). During abrasion, sanding and aging processes particles smaller than 100 nm were released. However, the nanoparticles that had been added remained firmly embedded in the binder matrix. The studies simulated everyday use of coated surfaces (parquet floor) by means of abrasion tests, the removal of old coatings by means of peripheral-longitudinal surface grinding (DREMEL), the influence of aging processes and the influence of climatic factors on surface weathering. Amongst other aspects, the release of TiO₂ nanomaterials from coatings that had been applied to different surfaces (wood, plastics, bricks) was investigated. Also, the influence of different types of stress (e.g. climatic stress, mechanical stress) was tested. Particle size distributions between 15 and 616 nm with a maximum of 630 particles per cm³ of air were measured (Hsu and Chein 2007). A release of isolated TiO₂ nanoparticles was not detected. As far as particle size distribution was concerned, there was no significant difference between coating systems with nanomaterials and those without them. In general, experts believe that a release of isolated nanoobjects from coatings is only possible by prior chemical or thermal degradation of the matrix material and not by mechanical treatment (Göhler et al. 2013). However, it still needs to be clarified if nanomaterial-containing matrix material once it is released into the environment undergoes any processes, which could lead to further degradation and subsequently to a release of isolated nanomaterials.

A release of nanomaterials (for example, photochemically degradable materials) during the weathering of their carrier matrix seems to be possible. Studies (Kaegi et al. 2008, Kaegi et al. 2010) have shown that weathering processes may release small amounts of synthetic TiO₂ particles ranging from 20 to 300 nm in size or nanosilver particles below 15 nm in size from facade paint. These particles may enter the environment via stormwater drains. Nano-TiO₂ does not leach out from dry coatings. However, it may get released into the breathable air together with the binder by normal wear and tear (Kaegi et al. 2008).

2. Environmental and Health Aspects

2.1 Potential environmental benefits

Coatings are primarily intended to protect buildings, machinery, vehicles and everyday objects. Applied on metal, wood and other surfaces they make a significant contribution to resource conservation by extending the life span and the replacement intervals of buildings, equipment and everyday objects.

Nanocoating systems may reduce environmental pollution even further (Steinfeldt et al. 2004). Nanocoatings produce thinner coating layers. For example, users of nano-based lacquer often need only 1/10 of the amount of conventional lacquer. This saves raw materials. Thus, the trend to design lighter-weight products can bring environmental benefits in the use stage, particularly in the transportation sector. Strong positive effects are anticipated not only in the automotive industry but also in the aircraft and rail industries. Another potential environmental benefit could be the minimization or substitution of solvents and toxic compounds used in paints and lacquers (e.g. chromium compounds).

Self-cleaning or easy-to-clean surfaces may reduce the need for cleaning. Especially in industrial cleaning self-cleaning or easy-to-clean surfaces may reduce the consumption of energy and cleaning agents and extend the life span of coated objects. UV-curable coatings are based on inorganic-organic binder. They are able to dry under UV light within seconds, thus reducing the energy input during the drying process. Also, UV-curable coatings typically contain no or less volatile solvents.

In principle, a number of environmental benefits are to be expected from nanomaterial-containing coatings. However, there are currently no reliable quantitative data available regarding the actual potential for environmental benefits. Descriptions of the environmental benefits of nanocoatings usually do not include any analysis or evaluation of the raw material and energy savings that can be made during production or any evaluation of the materials' fate and behaviour in their end-of-life phase (waste phase).

2.2 Environmental impacts

The environmental risks posed by coatings containing nanomaterials that are firmly embedded in a carrier matrix are currently considered to be small because the release of isolated nanomaterials is rather limited. Up to now there is no indication that nano-based surface coatings may pose a risk to the environment. However, it cannot be excluded that nanomaterials contained in coatings can be released, for example, by aging processes,

as described in Section 1.4 already. Laboratory studies using simulated solar radiation show that photo-catalytically active TiO₂ has a toxic effect on aquatic organisms due to the production of free oxygen radicals (Ma et al. 2012). Nanosilver, which is another nanomaterial used in coatings, is primarily applied for its antibacterial effect. Due to the release of silver ions it inhibits the growth of microorganisms. Colloidal silver has a toxic effect on aquatic organisms and is therefore classified as "Very hazardous to water" (Water Hazard Class 3). Numerous studies have shown aquatic toxic effects of nanosilver. In addition, effects on soil organisms were detected (Asghari et al. 2012, Bilberg et al. 2012, Wang et al. 2012, Schlich et al. 2013, Voelker et al. 2013, Ribeiro et al. 2014). The toxic effect of nanoscale silver that was detected during these studies was mainly triggered by the released silver ions. However, the release of silver ions depends on the stability, shape and coating of the nanosilver as well as on the surrounding environmental conditions (Gondikas et al. 2012, Kennedy et al. 2012, Tejamaya et al. 2012). In addition, there are studies that suggest an additional effect by the nanoparticles themselves (Bilberg et al. 2012). This needs to be taken into account when looking at potential long-term effects. Ecotoxicological data are also available for other nanomaterials that may be contained in coatings, for example, nanoscale zinc oxide, iron oxide and carbon black. However, as with nanoscale TiO₂ and silver, there is not sufficient information available regarding possible adverse effects to come to a final conclusion, in particular with regard to long-term exposure.

No information is available on current environmental concentrations of nanomaterials used in coatings. However, newly developed coating products containing nanomaterials should be designed in such a way that throughout their entire life cycle the release of nanomaterials into the environment is avoided to the maximum extent possible.

2.3 Health impacts

According to the current state of knowledge, the intended use of products, which are coated with nanomaterials that are firmly embedded in a matrix, does not pose a quantifiable nano-specific health risk to the consumer. Potential health risks mainly result from the inhalation of dust during the manufacture and further processing of nanomaterials, or when grinding, cutting, drilling or milling nanocoatings. If not done properly, spray painting may put the health of the user at risk. Aerosol sprays generate aerosols (very fine liquid droplets) that range from several dozens of nanometres to about 100 micrometres in size. Droplets less than 10 micrometres in size can penetrate deep into the lungs, possibly even reach the pulmonary alveoli. Inhaling surface-active substances from impregnating sprays may lead to alveolar collapse (BAG 2007). Therefore, the inhalation of spray mist from such products should always be avoided, independent of

whether they contain conventional surface-active substances or have been labelled by their manufacturers as nanotechnology-based products. The instructions for their safe use have to be closely followed. Under no circumstances should they be used in enclosed places.

Only few studies (TiO₂ and carbon black) are available on the chronic inhalation toxicity of synthetic nanomaterials. These studies have shown clear effects in rats such as inflammatory reactions and tumours. However, it is currently still being debated whether primary genotoxic effects or the consequences of overloading and inflammation are responsible for the carcinogenicity of certain nanomaterials. Also unclear is if adverse effects are to be expected in the low-dose range that is relevant for the environment. The Federal Ministry for the Environment (BMUB) and BASF as industrial partner have therefore initiated a comprehensive chronic in-vivo inhalation project on rats. During the project the effect of different concentrations of nanoscale cerium dioxide (Nano-CeO₂) is analysed. The project is planned for four years. The project follows the testing guidelines of the Organisation for Economic Co-operation and Development (OECD). The Federal Environment Agency (UBA), Federal Institute for Risk Assessment (BfR) and Federal Institute for Occupational Safety and Health (BAuA), as independent technical authorities, will review and evaluate the results of the study (See also BMUB Press Release No. 066/12 dated 15 May 2012).

Exposure to nanomaterials may also occur through dermal absorption during the production and use of nanomaterial-containing lacquers and paints or during the degradation of matrix material in existing nanocoatings. Numerous studies have shown that healthy and intact skin is a good barrier against TiO₂ and ZnO nanoparticles used in sunscreen: The nanoparticles remained in the uppermost layers of the horny layer ("stratum corneum") or were transported back to the surface of the skin and then rubbed off (EU Project "Nanoderm"⁹). However, there are indications that other types of nanoparticles can enter deeper layers of skin: For example, gold nanoparticles (5 nm in diameter) penetrated the horny layer of intact mouse skin (Huang et al. 2010) and quantum dots¹⁰ (Ø 4.5 nm – 12 nm) penetrated into the dermis of pig skin (Ryman-Rasmussen et al. 2006). Currently there is no indication that nanoparticles that small can be released as free particles from lacquers or paints.

For coatings that contain nanosilver it is not yet clear if their uncontrolled, large-scale and low-dosage application in everyday products could result in an increased selection of silver-resistant microorganisms. Since silver resistance genes and antibiotic resistance genes in bacteria are often located on the same plasmids and can be passed on to other bacteria, this

⁹ NANODERM - Quality of Skin as a Barrier to Ultra-Fine Particles. This research project was funded by the European Commission. Project ID: QLK4-CT-2002-02678 (Butz et al. 2007)

¹⁰ A quantum dot is a nanoscopic material structure that often consists of semiconductive material.

may (under certain selection conditions) result not just in resistance to silver but also in resistance to antibiotics in strains that have not been resistant before (BfR press release No. 08/2012 dated 27 Feb 2012).

3. Legal Framework

Manufacturers of lacquers and paints are currently not required to label products that contain nanomaterials as nanoproducts.

The use of biocides in coatings is subject to the EU Biocides Regulation (EU Regulation No. 528/2012), which has been in force since September 2013. The biocides regulation contains specific rules for nanomaterials: Where a biocidal product contains nanomaterials, the risk posed by these materials to human health, animal health and the environment has to be assessed. In addition, the labels of biocidal products must indicate the names of all active biocidal substances and all nanomaterials contained in the biocidal product followed by the word „nano“ in brackets. Within the biocides regulation the definition of the term "nanomaterial" recommended by the EU Commission has become legally binding.

In principle, nanomaterials are also covered by the European chemicals regulation REACH. However, the current version of REACH does not contain nano-specific requirements regarding data collection and risk assessment. Various options for amendment are being discussed at European level. The federal agencies (BAuA, BfR and UBA) too have developed a joint concept on this topic (UBA et al. 2013).

As far as occupational health & safety is concerned, the Federal Institute for Occupational Safety and Health (BAuA) and the German Chemical Industry Association (VCI) have issued a guidance document for handling and using nanomaterials at the workplace (BAuA-VCI 2012). The German paint and printing ink industry association (VdL) has published a branch-specific guidance for the safe handling of nano-objects at the workplace (VdL 2010).

It cannot be ruled out that nanomaterials are washed out from wastes that are covered with nanomaterial-containing coatings and thus released into the environment. According to the Federal Waste (Recycling) Act (KrWG) the waste producer remains responsible for his/her waste until its final disposal.

4. Consumer information tools

There is considerable uncertainty amongst consumers as to whether products advertised with the word „nano“ actually contain nanomaterials. There are no binding labelling or reporting requirements for coatings that contain nanomaterials, unless they fall within the scope of the EU Biocide Regulation. Discussions held amongst the various stakeholders in Germany and at European level with respect to the need for such tools to improve transparency are controversial. Several European Member States have introduced a national register for products containing nanomaterials or are in the process of doing so. However, these and other Member States would rather prefer a Europe-wide register. The EU Commission is currently still reviewing the option of introducing a European register for nanoproducts. In June 2012 UBA has published a concept for a semi-public European register for products containing nanomaterials (UBA 2012).

5. Research and development needs

Further research and development needs arise with respect to the exposure to and environmental behaviour of nanomaterials in coatings, their toxicological effects on humans and the environment, and the sustainability of such coatings. From an environmental point of view, there are therefore wide-ranging needs in terms of research and development.

It is required to

- ▶ Develop and adapt suitable standardized testing and analytical methods for measuring the exposure to nanomaterials from coatings in the various environmental media (water, soil, air) - taking into account that nanomaterials are typically not released into the environment as isolated nanoparticles but may be embedded in or attached to the coating material;
- ▶ Develop and adapt test guidelines that ensure the comparability of research findings regarding the environmental impacts and behaviour of nanomaterials;
- ▶ Develop methods that detect the release of nanomaterials throughout the entire life cycle of products that are coated with nanomaterials including their use and disposal; perform individual case studies of nanomaterials across the entire life cycle of the products: Determine their stability in the coatings and their fate and behaviour in the environment, for example, after weathering or abrasion;
- ▶ Investigate the biopersistence (in particular in the lungs), bioavailability and (eco)toxicity of nanomaterials used in coatings;

- ▶ Perform life-cycle analyses assessing the impacts of nanomaterial-containing coatings on the environment and human health throughout the entire product life cycle to be able to evaluate their benefits and compare them to conventional products. The findings from these assessments can then be used for the development of environmentally compatible coatings;
- ▶ Study the disposal of nanomaterial-containing coatings such as incineration or recycling, since there is only little knowledge available about the behaviour and release of nanomaterials and their impact on these processes, and, if necessary, develop concepts for their proper disposal.

6. Conclusions

Following the precautionary principle, novel applications should generally be tested for safety with regard to human health and the environment before they are marketed. A risk assessment is to exclude concern or show risk management measures with which the risk can be reduced to an acceptable level.

In the opinion of the Federal Environment Agency the environmental compatibility of nanomaterials and their applications are an important aspect when discussing the opportunities and risks they pose. This is particularly true when nanomaterials come into direct contact with humans or are released into the environment during their life cycle. While there is some information available about the toxicological and ecotoxicological properties of the nanomaterials used, this information is often incomplete and not comparable making final assessment of the risks impossible. Therefore, the basic principle that nanomaterials in coatings are the safer for the environment and human health the more firmly they are embedded in the coatings should be considered in their manufacture.

A number of environmental benefits are to be expected from nanotechnology-based coatings, for example, thinner coating layers, minimization or substitution of solvents and toxic compounds used in paints and lacquers (e.g. chromium compounds). In addition, self-cleaning or "easy-to-clean" surfaces may minimize the need for cleaning, reduce the consumption of energy and cleaning agents and extend the life span of the coated objects. However, to ensure the safety of coatings that contain nanomaterials, studies should be performed at an early stage of their development already that look not only at the environmental benefits but also at the risks posed by nanomaterials and their applications. The Federal Environment Agency recommends the development and standardization of suitable measuring and analytical methods that allow a better detection and precise exposure estimation. Before they are marketed already, coatings

should be tested with respect to the potential release of nanomaterials across their entire life cycle. In addition, their ecological sustainability with special consideration of material flows, energy consumption, waste and emissions should be investigated.

There is currently no comprehensive information available about the forms in which nanomaterials in coatings are present in the market. To provide transparency about nanomaterial-containing coatings for the various players in the value chain and the consumers, at least those products for which the release of nanomaterials (see definition on page 1) across their entire life cycle cannot be ruled out, should be notified to a register.

Consumers should be informed about the potential environmental benefits and risks of coatings that contain nanomaterials and about special handling requirements. Researchers, product designers, consumers and decision makers should continue to share information last but not least to protect the environment.

7. Sources and references

- Asghari, S., Johari, S.A., Lee, J.H., Kim, Y.S., Jeon, Y.B., Choi, H.J., Moon, M.C., Yu, I.J. (2012): *Toxicity of various silver nanoparticles compared to silver ions in Daphnia magna*. J Nanobiotechnology 10, 14.
- BAG (2007): *Treibgassprays: ein Gesundheitsrisiko?* Bundesamt für Gesundheit (BAG) Schweiz, 12/07.
www.bag.admin.ch/themen/chemikalien/00228/04394/index.html?lang=de
- BAuA-VCI (2012): *Empfehlung für die Gefährdungsbeurteilung bei Tätigkeiten mit Nanomaterialien am Arbeitsplatz*.
http://www.baua.de/de/Publikationen/Fachbeitraege/Gd4.html;jsessionid=F8436F0141A96907EC623477C6CCE38B.1_cid380
- BG BAU (2013): *Nano-Liste der BG BAU – Nanoteilchen in Bau- und Reinigungsprodukten*. Stand 28.03.2013.
<http://www.bgbau.de/praev/fachinformationen/gefahrstoffe/nano/pdf-files/nano-liste.pdf>
- Bilberg, K., Hovgaard, M.B., Besenbacher, F., Baatrup, E. (2012): *In Vivo Toxicity of Silver Nanoparticles and Silver Ions in Zebrafish (Danio rerio)*. J Toxicol 2012, 293784.
- Butz, T. et al. (2007): *NANODERM - Quality of Skin as a Barrier to ultra-fine Particles*. Final Report. <http://www.uni-leipzig.de/~nanoderm/Downloads/downloads.html>
- Deutsches Lackinstitut (2011): *Nanolack-Studie – Entweichen Nanoteilchen aus dem Lack?* Lack im Gespräch, Informationsdienst Deutsches Lackinstitut Nr. 110, Seite 9-11. http://www.lacke-und-farben.de/fileadmin/templates/img/pdf/LIG_110.pdf
- Deutsches Lackinstitut (2012): *Brandschutz-Beschichtungen – 40 Minuten können Leben retten*. Lack im Gespräch, Informationsdienst Deutsches Lackinstitut Nr. 112, Seite 5. http://www.lacke-und-farben.de/fileadmin/templates/img/pdf/LIG_112.pdf
- Goedicke, S. (2009): *High temperature protection – Novel pigments in sol-gel coatings inhibit corrosion at up to 1300°C*. European Coatings Journal 09/2009, pp.34-37.
- Göhler, D., Stintz, M., Hillemann, L., Vorbau, M. (2010): *Characterization of nanoparticle release from surface coatings by the simulation of sanding process*. Ann. Occup. Hyg., 54 (6), 615-624, 2010.
<http://annhyg.oxfordjournals.org/content/54/6/615.abstract>
- Göhler, D., Nogowski, A., Fiala, P., Stintz, M. (2013): *Nanoparticle release from nanocomposites due to mechanical treatment at two stages of the life-cycle*. J. Phys.: Conf. Ser. 429 012045. DOI: 10.1088/1742-6596/429/1/012045.
- Gondikas, A.P., Morris, A., Reinsch, B.C., Marinakos, S.M., Lowry, G.V., Hsu-Kim, H. (2012): *Cysteine-Induced Modifications of Zero-valent Silver Nanomaterials: Implications for Particle Surface Chemistry, Aggregation,*

Dissolution, and Silver Speciation. Environmental Science & Technology 46(13), 7037-7045.

Greßler, S., Fiedeler U., Simkó M., Gazzó A., Nentwich M. (2010): *Selbst-reinigende, schmutz- und wasserabweisende Beschichtungen auf Basis von Nanotechnologie*. ÖAW-ITA-Nanotrust dossiers Nr. 020, Juli 2010.

Guiot, A., Golanski, L., Tardif, F. (2009): *Measurement of nanoparticle removal by abrasion*. Journal of Physics: Conference Series 170 (2009) 012014, Doi: 10.1088/1742-6596/170/1/012014.

Hofmann, T. (2006): *Nanobeschichtung für Architektur- und Solargläser – Smart Glazing*. In Luther und Zweck (2006).

Hsu, L., Chein, H. (2007): *Evaluation of nanoparticle emission for TiO₂ nanopowder coating materials*. Journal of Nanoparticle Research 2007;9:157–63

Huang, Y., Yu F., Park Y.S. et al. (2010): *Coadministration of protein drugs with gold nanoparticles to enable percutaneous delivery*. Biomaterials 31, 9086–91.

Kaegi, R., Ulrich, A., Sinnet, B., Vonbank, R., Wichser, A., Zuleeg, S., Simmler, H., Brunner, S., Vonmont, H., Burkhardt, M., Boller, M. (2008): *Synthetic TiO₂ nanoparticle emission from exterior facades into the aquatic environment*. Environmental Pollution 156, 233-239.

Kaegi, R., Sinnet, B., Zuleeg, S., Hagendorfer, H., Mueller, E., Vonbank, R., Boller, M., Burkhardt, M. (2010): *Release of silver nanoparticles from outdoor facades*. Environmental Pollution 158, 2900-2905.

Kennedy, A.J., Chappell, M.A., Bednar, A.J., Ryan, A.C., Laird, J.G., Stanley, J.K., Steevens, J.A. (2012): *Impact of organic carbon on the stability and toxicity of fresh and stored silver nanoparticles*. Environ Sci Technol 46(19), 10772-10780.

Leuninger, J., Tiarks, F., Wiese, H., Schuler, B. (2004): *Wässrige Nanokomposite*. Farbe & Lack 10/2004 S. 30. <http://www.european-coatings.com>.

Luther, W., Zweck, A. (2006): *Innovationsbegleitung Nanotechnologie: Nanotechnologie in Architektur und Bauwesen*. Zukünftige Technologien Nr. 62

Ma, H., Brennan, A., Diamond, S.A. (2012): *Phototoxicity of TiO₂ nanoparticles under solar radiation to two aquatic species: Daphnia magna and Japanese medaka*. Environ.Toxicol.Chem. 31(7), 1621-1629.

Paschen H., Coenen C., Fleischer T., Grünwald R., Oertel D., Revermann C. (2003): *TA-Projekt Nanotechnologie Endbericht*. Büro für Technikfolgen-Abschätzung beim Deutschen Bundestag (TAB).

Ribeiro, F., Gallego-Urrea, J.A., Jurkschat, K., Crossley, A., Hassellöv, M., Taylor, C., Soares, A.M.V.M., Loureiro, S. (2014): *Silver nanoparticles and silver nitrate induce high toxicity to Pseudokirchneriella subcapitata, Daphnia magna and Danio rerio*. Science of The Total Environment 466–467(0), 232-241.



Rössler, A. (2007): *Nanotechnologie in der Farben und Lackindustrie*. <http://www.aktuelle-wochenschau.de/2007/woche17/woche17.html> (Abruf 08.03.2012)

- Ryman-Rasmussen, J.P., Riviere, J.E., Monteiro-Riviere, N.A. (2006): *Penetration of intact skin by quantum dots with diverse physicochemical properties*. *Toxicol.Sci.* 91(1): 159-165.
- Schlich, K., Klawonn, T., Terytze, K., Hund-Rinke, K. (2013): *Effects of silver nanoparticles and silver nitrate in the earthworm reproduction test*. *Environ Toxicol Chem* 32(1), 181-188.
- Steinfeldt, M., v.Gleich, A., Petschow, U., Haum, R., Chudoba, T., Haubold, S. (2004): *Nachhaltigkeitseffekte durch Herstellung und Anwendung nanotechnologischer Produkte*. Schriftenreihe des IÖW 17704. Berlin.
http://www.bmbf.de/pub/nano_nachhaltigkeit_ioew_endbericht.pdf
- Tejamaya, M., Römer, I., Merrifield, R.C., Lead, J.R. (2012): *Stability of Citrate, PVP, and PEG Coated Silver Nanoparticles in Ecotoxicology Media*. *Environmental Science & Technology* 46(13), 7011-7017.
- Umweltbundesamt (2012): *Konzept für ein europäisches Register für nanomaterialhaltige Produkte*.
<http://www.umweltbundesamt.de/publikationen/konzept-fuer-ein-europaeisches-register-fuer>
- Umweltbundesamt, Bundesinstitut für Risikobewertung, Bundesanstalt für Arbeitsschutz und Arbeitsmedizin (2013): *Nanomaterialien und REACH – Hintergrundpapier zur Position der deutschen Bundesbehörden*.
<http://www.umweltbundesamt.de/publikationen/nanomaterialien-reach>
- VdL (2010): *VdL-Leitfaden für den Umgang mit Nanoobjekten am Arbeitsplatz*. Verband der deutschen Lack- und Druckfarbenindustrie e.V., Juni 2010.
- VdL (2013): *Jahresbericht 2012/2013*. Verband der deutschen Lack- und Druckfarbenindustrie e.V.
http://www.lackindustrie.de/Publikationen_/VdL-Jahresberichte/Seiten/Jahresbericht-2013.aspx
- Voelker, C., Boedicker, C., Daubenthaler, J., Oetken, M., Oehlmann, J. (2013): *Comparative toxicity assessment of nanosilver on three Daphnia species in acute, chronic and multi-generation experiments*. *PLoS One* 8(10), e75026.
- Vorbau, M., Hillemann, L., Stintz, M. (2009): *Method for the characterization of the abrasion induced nanoparticle release into air from surface coatings*. *Journal of Aerosol Science* 40/3, S. 209-217
- Wang, Z., Chen, J., Li, X., Shao, J., Peijnenburg, W.J. (2012): *Aquatic toxicity of nanosilver colloids to different trophic organisms: contributions of particles and free silver ion*. *Environ Toxicol Chem* 31(10), 2408-2413.

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