FACT SHEET NANO PRODUCTS

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Use of Nanomaterials in Textiles

1 Application description

1.1 Products and purpose of using nanomaterials[1]

The textile industry is one of the most important consumer goods industries worldwide. Its mostly small and medium-sized enterprises produce textiles for various uses such as clothing, home textiles (such as bed and table linen, kitchen towels and cleaning rags), household textiles (such as curtains, furniture fabrics, textile floor coverings) and technical textiles (such as protective clothing, vehicle seat covers, tarps, tire fabrics, filter materials).

In Germany, about 60 institutions and companies work in the field of nanotechnical textile processing (BMBF, 2011). The German textile industry wants to generate added value that may by far exceed the basic use by integrating new functionality into textile materials, which is to secure the industry a competitive edge (Paschen et al., 2003). These include, for example, improved dirt and water repellent properties, breathability, UV protection, or resistance to wear of the textiles. Nanotechnical manufacturing and finishing processes hold the promise of economic and ecological benefits (Gesamtverband textil+mode 2011). There is already a rapidly growing number of textiles with dirt and water repellent or antimicrobial properties and UV protection offered in the market, and their product description states that they were produced using nanomaterials[2] (BMBF 2011).

1.2 Nanomaterials contained in textiles

The nanomaterials that are and soon will be used most frequently in textiles are: Silver, silicon dioxide, titanium dioxide, zinc oxide, aluminum (hydr)oxides, nanoclay (primarily montmorillonite), carbon nanotubes, carbon black. Copper, gold, iron (hydr)oxides, polypyrrol, and polyaniline are of secondary priority (Som et al., 2010). Table 1 provides an overview of potential properties that are achieved by using various nanomaterials.

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

[2] For example, about 15 percent of the entries in the international database for nanomaterial-containing consumer products kept by the Woodrow Wilson Center are garment applications (www.wilsoncenter.org/)
The BUND database provides information on nano-containing textiles:
http://www.bund.net/themen_und_projekte/nanotechnologie/nanoproduktdatenbank/

Table 1: Nanomaterials used in textiles and their function (based on Bickel and Som, 2011; Gressler et al., 2010; Gesamtverband textil+mode, 2011)

Properties of nanotextiles	Nanomaterial
Electroconductive/antistatic	Carbon black Carbon nanotubes (CNT) Copper Polypyrrol Polyaniline
Increased durability	Aluminum oxide CNT Polybutyl acrylate Silicon dioxide Zinc oxide
Antimicrobial	Silver Chitosan* Silicon dioxide* Titanium dioxide* Zinc oxide*
Self-cleaning/dirt and water repellent	CNT Fluoroacrylate Silicon dioxide Titanium dioxide (anatase)
Moisture-absorbent	Titanium dioxide
Improved dyeability	Carbon black Nanoporous hydrocarbon-nitrogen coating Silicon dioxide
UV protection, protection from fading	Titanium dioxide (rutile) Zinc oxide
Fire resistance	CNT Boroxosiloxane Montmorillonite (nanoscale clay) Antimony ash
Controlled release of active ingredients, pharmaceuticals, or fragrances	Nanostructured hollow bodies (e.g. cyclodextrine-based) Montmorillonite (nanoscale clay) Silicon dioxide
Heat conducting or insulating properties	CNT Vanadium dioxide
Shielding electromagnetic radiation (IR / microradiation / radio waves)	Indium tin oxide
Abrasion resistance	CNT

* Chitosan, silicon dioxide, titanium dioxide, and zinc oxide are mentioned in the references specified for antimicrobal properties in textiles. It should be pointed out that these substances are either not notified in the EU's existing active biocidal substances process or are listed in Annex I to the Biocidal Products Directive. They may therefore neither be used in this function nor advertised as antimicrobial in textiles.

1.3 Manufacture

The desired function of the textiles can be achieved by introducing synthetic nanomaterials or by nanostructuring.

When using nanomaterials in the manufacturing and finishing process, these materials are either integrated into the fiber volume or applied as a coating onto the textile (see Figure 1) (Som et al., 2009).

Figure 1: Ways of embedding nanomaterials in textiles (based on Bickel and Som 2011)

In the core or sheath fiber

On the fiber or in the coating

Textiles that consist of nanostructures may be fibers with a diameter in the nanoscale range or fibers and coatings with nanopores (see Figure 2).

Figure 2: Nanostructured materials (based on Bickel and Som 2011)

Nanofibers (nanoscale diameter)

Nanopores (in the fiber or coating)

Nanolayers on the fiber

1.4 Stability of the nanomaterials in the textiles

The nanomaterials are to be stably embedded to maintain the product quality and functionality of the textiles. This also prevents the release of nanomaterials with potential hazards to human health and the environment.

The release of the nanomaterials from the textiles depends on the following parameters (Bickel and Som 2011):

- The integration site into the textile (e.g. into the sheath or core of the fiber, into the coating)
- Type and strength of the bond between nanomaterials and textile fibers (e.g. a covalent bond)
- Textile properties such as abrasion resistance and flexibility of the coating.

A general quantitative statement regarding the release of nanomaterials from textiles cannot currently be made. Existing data was obtained from modeling and are individual case studies.

Conventional textiles lose between 5% and 20% of their weight during their use phase, e.g. through laundry, exposure to sunlight, or mechanical abrasion. It can therefore be assumed that nanomaterials integrated into, or applied onto, textiles will enter the environment in free or bound form. Studies of the behavior of nanomaterials in textiles show that nanomaterials (nanosilver and nano titanium oxide) are released from textiles during laundry, depending on the way they are integrated. Release during laundry varies from almost zero to almost 100% (Geranio et al. 2009; Benn and Westerhoff 2008; Windler et al. 2012; Tonning et al. 2012).

2 Environmental and health aspects

A general conclusion on potential risks with regard to human health and the environment can currently not derived due to the diversity of nanomaterial-containing textiles with respect to manufacturing processes, the synthetic nanomaterials used, and their uses. Some of the nanomaterials used have the potential for toxic or ecotoxic effects but these nanomaterials must be relevantly absorbed into the system to act in this way.

Since 2009, the "Working Party on Manufactured Nanomaterials" by the Organization for Economic Cooperation and Development (OECD) has subjected 13 selected, market-relevant nanomaterials to an international testing program ("OECD Sponsorship Program") for a systematic study of their toxicology, ecotoxicology, and environmental behaviour. The goal of this international effort is the collection of data on the behavior and action of nanomaterials and the development of adequate testing methods for nanomaterials. Germany takes an active part in this program and supports it with project findings from the environmental research plan coordinated by the Federal Environment Agency (UBA) and other national research projects.

Numerous national and international projects currently deal with problems regarding the safety of nanofunctionalized textiles. Examples include the "TechnoTox" project sponsored by the State of Baden-Württemberg since 2010 and the BMBF-sponsored joint project titled UMSICHT[3]. The latter project, in which UBA participates as well, includes the determination of the silver content in abrasion residues from real textile products. At the same time, the project studies the behaviour and ecotoxicity of nanosilver in various scenarios.

2.1 Environmental compatibility of the products

Major aspects for the environmental compatibility of nanomaterials in textiles are raw material quantities used and the release of nanomaterials into the environment over the entire life cycle of the textile.

There are only a few life cycle analyses of textiles containing nanomaterials. The studies published do not make transparent statements or no statement at all on energy consumption and raw material quantities used. One study (Walser et al. 2011) investigated the greenhouse gas potential based on the CO_2 footprint as the key indicator, and the toxicity of various biocidal ingredients (nanosilver, triclosan) in textiles, using T-shirts as examples. The findings show that the ecotoxicity of the T-shirts increases during washing if biocidal substances, either triclosan or nanosilver, are added. The authors recommend the analysis of other impact categories, such as the CO_2 footprint, for comparison. While this footprint increases, as expected, in the production phase of T-shirts with nanosilver, it can drop significantly compared to biocide-free T-shirts in the use phase – depending on the consumers' environmentally conscious

[3] UMSICHT = **Um**weltgefährdung durch **Si**lber-Nanomaterialien: vom **Ch**emischen Partikel bis zum **T**echnischen Produkt (Assessment of the environmental hazard by silver nanomaterials: from chemical particles to a technical product)

behavior – (from 402 kt CO_2/year down to 47 kt CO_2/year [4]). The study shows that the use phase of the textile can make an important contribution to saving energy if the consumers adjust their laundry behavior to the fact that textiles with active biocidal ingredients need fewer washing cycles, which saves power and laundry detergents. Another example (BMU 2011) finds that the UV protection caused by nanomaterials can help to improve the durability of the textiles (such as awnings) and therefore to establish a longer life cycle of the respective product.

Self-cleaning surfaces can also result in saving laundry cycles and detergents. Improved dyeability of textiles reduces the number of dyeing and washing cycles and can therefore save raw materials and prevent wastewater. Note that such examples that manufacturers and traders describe as "beneficial" for the environment and human health have not been corroborated by data, yet.

The main sources of introducing nanomaterials from textiles into the environment are textile finishing processes in the manufacturing phase, laundry processes in the use phase, and disposal. In the processes mentioned first, the nanomaterials can enter wastewater treatment plants via industrial and urban wastewater. The extent to which they are removed from the water cycle with the sewage sludge has as yet been studied for a few nanomaterials only. No generally valid and final statements can currently be made on this topic. One study shows that silver ions that are released from silver particles into the environment can form nanoscale silver particles under certain conditions (Glover et al. 2011). The currently available findings suggest that typically more than 90% of the nanomaterials investigated, such as TiO_2, ZnO, silver, or CeO_2, are separated via the sewage sludge (Limbach et al. 2008; Simkó and Fries 2012; Burkhardt et al., 2010, Nickel et al. 2012). No severe impairment of the nitrification performance of microorganisms in the activated sludge of wastewater treatment plants has been observed as yet. However, further studies should take plants and soil-dwelling organisms into account since 30% of the sewage sludge in Germany are used in agriculture (Destatis 2012). As yet unpublished studies conducted on behalf of UBA showed effects on soil-dwelling organisms from nanoscale TiO_2 and silver. Other studies found toxic effects on pumpkins by nanoscale copper and silver (Musante and White 2012). The toxic effects of nanoscale silver that were found are mainly caused by released toxic silver ions. The release of these silver ions is largely determined by the stability of the nanoscale silver. This again is dependent on the shape and coating of the particles but also on the surrounding environmental medium (Tejamaya et al. 2012, Gondikas et al. 2012, Kennedy et al. 2012). In addition to a change in toxic effect of nanomaterials, the uptake and accumulation processes may be changed as well if substances are present in the nanoscale range (Khan et al. 2012).

Since more and more nanomaterials are released into the environment, further studies will be required on their behavior in the soil, their uptake and accumulation in plants and soil-dwelling organisms.

Disposal in incinerators must be viewed as another input path of nanomaterials from textiles. A study that looked into the behavior of CeO_2 nanoparticles in a waste incineration plant has found that nanoparticles do not escape into the atmosphere if the incineration plant is technically well-equipped (filters, etc.) but that they attach themselves to residues and can then be found in landfills or recycled raw materials (Walser et al. 2012).

[4] The statistics refer to Switzerland (population 8.1 million), and it is assumed that every person has five T-shirts.

2.2 Health-related aspects

As far as nanomaterials are released from textiles, the main intake paths during manufacture and use are dermal or inhalative.

Dermal intake

Numerous skin penetration studies show that healthy intact skin is a good barrier for such TiO_2 and ZnO nanoparticles that are also used in sun protection lotions: The nanoparticles remained in the upper layers of the stratum corneum or were deposited in the hair follicles. Since the hairs grew, the particles were transported from there back to the surface of the skin after a few days and rubbed off (Nanoderm EU project). But there are indications from intact animal skin that other nanoparticles can enter deeper layers of the skin: For example, gold nanoparticles (5 nm in diameter) penetrated the horny layer of mouse skin, and quantum dots[5] (Ø 4.5 nm – 12 nm) penetrated into the dermis after application onto pig skin (Ryman-Rasmussen et al. 2006). Thus the skin in principle provides an entrance gate for the transport of nanoparticles or ions released from them into other organs of the body (e.g. via the bloodstream, neuronal transport). It is not yet known if such small nanoparticles are released from textiles and what concentrations we have to assume.

Two essential questions relating to the health assessment of textiles containing nanosilver have not yet been finally clarified: 1. How does nanosilver contained in textiles act on the natural skin flora and the associated physiological equilibrium in the long term; 2. Does the uncontrolled large-scale and low-dosed use of silver and nanosilver in everyday products result in the selection of silver-resistant microorganisms. Since silver and antibiotic resistance genes in bacteria are often located on the same plasmids and can be passed on to other bacteria, selection conditions could result not just in resistance to silver but also to antibiotics in strains that had not been resistant before (BfR press release 08, 27/02/2012). These unsettled questions have caused the Federal Institute for Risk Assessment (BfR) to recommend that silver (and nanosilver) should not be used widely as antimicrobial substances outside of clinical applications in consumer products. This opinion is shared by the Federal Environment Agency.

Inhalative intake

There are only few studies available on the chronic inhalation toxicity of synthetic nanomaterials (TiO_2 and carbon black). These studies were conducted at unrealistically high concentrations in rats and show clear effects such as inflammatory reactions and tumors. It is currently debated whether primary genotoxic effects or the consequences of overloading and inflammation are mechanically responsible for the carcinogenicity of certain nanomaterials. It is also unclear if effects should be expected in the low-dose range that is relevant for the environment. The Federal Ministry for the Environment (BMU) and BASF as industrial partner have therefore initiated a comprehensive chronic in vivo study in the rat that tests various concentrations of nano-CeO_2. Nano-CeO_2 is considered a representative of the group of granular biodurable dusts of relatively low toxicity that also includes TiO_2 and aluminum oxide. The study is planned for four years and guided by OECD testing specifications. UBA, BfR, and the Federal Institute for

[5] A quantum dot is a nanoscopic material structure that often consists of semiconducting material.

Occupational Safety and Health (BAuA) will perform follow-up and analyze the study as independent specialized authorities.

CNTs (carbon nanotubes) with a fiber length of more than 15 µm (long CNTs) are similar in structure to asbestos and other mineral fibers that have a proven carcinogenic potential if inhaled. The inhalation studies of up to 13 weeks conducted as yet with various CNTs showed that specific CNTs can cause inflammatory fibrotic lesions in the lungs that can lead to the formation of granulomas. Chronic studies have yet to be conducted. After the CNTs have entered the respiratory tract, individual tubes and agglomerates can settle and remain there. A research project on the intake, distribution and excretion of CNTs (mean length 5-10 µm) after inhalation by rats that was awarded by UBA and has not been completed yet showed that the CNTs migrated fast from the lung into the pleural cavity in the first days the rats were exposed to them. The CNTs were also carried off fast from there. It is assumed that, over time, these CNTs migrated via the bloodstream into the liver and kidneys where they were detected using a dark field microscope. The number of CNTs in the liver and kidneys was very small, however.

3 Legal framework

Textiles that do not just temporarily come into contact with the human body (clothing) are generally subject to the provisions of the German Foods, Consumer Goods and Feedstuffs Act (LFGB). The purpose of this act is to ensure the protection of consumers of foods, feedstuffs, cosmetics, and articles of daily use by preventing or averting a risk to human health. There are no specific legal regulations with respect to nanomaterials in textiles. There are also no regulations as yet for equipping textiles with TiO_2 as UV protection or with CNTs for greater strength of the fibers. In principle, manufacturers must guarantee the safety of their products under the European General Product Safety Directive (Art. 3 of the Product Safety Act). The manufacturers and distributors are responsible under the LFGB or the Product Safety Act that textiles equipped with nanomaterials pose no health risk for consumers.

Equipment of textiles with biocidal substances is regulated in the Biocidal Products Directive (98/8/EC). A new EU Biocidal Products Directive 528/2012 entered into force in July 2012 and has to be applied as of September 2013. The new Biocidal Products Directive expressly regulates nanomaterials and treated materials: If a biocidal product or a treated product contains nanomaterials, these have to be reviewed separately with respect to the risks they pose to human and animal health and the environment. In addition, the labels of biocidal products must indicate the biocidal ingredients used and the names of all nanomaterials contained in the biocidal products followed by “nano” in brackets. This is the first time that the definition of nanomaterials recommended by the EU Commission is implemented in a legally binding manner.

While the European REACH legislation on chemicals basically lists nanomaterials, there are no specific requirements with respect to the database and risk assessment. Various adjustment options are being discussed at European level. Also the higher federal authorities in Germany (BAuA, BfR, and UBA) have developed a joint concept for this.

4 Consumer information tools

There is great insecurity among consumers as to whether textile products advertised using the “nano” term actually are products treated with nanotechnology. Various manufacturers have decided to label their products voluntarily to make the marketing of textiles more transparent. For example, the Hohenstein Institutes offer the "Nanotechnology" quality seal that is awarded as a result of a test that evaluates if the functionality of textiles is based on nanotechnology and if these textiles are generally fit for use[6]. The Denkendorf quality seal for self-cleaning textiles is to confirm and certify the presence of specific surface structures, the resistance of the materials, and the self-cleaning effect[7]. Quality seals of this type help improve consumer information, which has been insufficient so far; it should be noted, though, that these are not certified seals and they do not confirm the harmlessness of a product for humans and the environment.

There is no binding labeling or reporting requirement for textiles containing nanomaterials unless these are covered by the new EU Biocidal Products Directive. Discussions among various groups of stakeholders with respect to the need for these tools to improve transparency are still controversial in Germany and at European level. UBA has published a concept for a semi-public European registry of products containing nanomaterials in June 2012.[8]

5 Research and development needs

The following research and development needs arise with respect to the environmental behaviour of nanomaterials contained in textiles, their impacts on humans and the environment, and the sustainability of such textiles:

It is required to

- Develop and adapt suitable standardized measuring, testing, and analytical methods for measuring the exposure to nanomaterials in various environmental compartments (water, soil, air);
- Develop and adapt test guidelines that ensure the comparability of research findings on the environmental impact and behaviour of nanomaterials;
- Develop methods that detect the release of nanomaterials during the use and disposal of textiles containing nanomaterials across their life cycle; individual case studies of nano-materials across their life cycles: Determine their stability in textiles, their environment-tal fate after discharge or abrasion, and the contact of humans with nanomaterials (exposure estimate). This individual analysis should also include a comparison with alternative non-nanoscale substances with similar functionality in textiles;
- Study the bioavailability and toxicity of such nanomaterials that are used in textiles;
- Perform life-cycle assessments of the advantages of textile products treated with nanomaterials compared to conventional products, including the impact on human health and the environment across the product life cycle;
- Study the disposal of textiles containing nanomaterials, e.g. incineration or recycling, since there is little knowledge about the behaviour and release of nanomaterials and

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[6] http://www.hohenstein.de/en/testing/material/effectiveness/effectiveness.xhtml (17/09/2012)

[7] http://www.itv-denkendorf.de/en/research-area/oberflaechentechnologien.htm (17/09/2012)

[8] http://www.umweltbundesamt.de/chemikalien/publikationen/information_concept_nanoregister_npr_e.pdf (17/12/2012)

their impact on the processes that take place. Optionally, develop concepts for proper disposal.

The knowledge generated in life cycle assessments can be used for developing sustainable textiles.

6 Conclusion

As a precaution, novel applications should generally be tested for safety with regard to human health and the environment before they are marketed. A comprehensive 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 uses 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, which can be expected for textiles equipped with nanomaterials. While there is some information available about the toxicological and ecotoxicological properties of the nanomaterials used, this information is often incomplete or not comparable, making final risk assessment impossible. The principle that nanomaterials in textiles are the safer for the environment and human health the more stable they are embedded should therefore be considered in their manufacture.

In addition to ways of protecting the environment, the risks posed by nanomaterials and their use should be studied at an early stage of development to ensure the safety of the textile product. The Federal Environment Agency recommends the development and standardization of suitable measuring and analytical methods that allow better detection and better exposure estimation. Textile products should be studied before they are marketed with respect to the potential release of nanomaterials across their entire life cycle. Ecological sustainability of the products, with special consideration of material flows, energy consumption, waste and emissions should be studied as well. 95 % of the textiles and fibers in the German market are produced outside of Germany. This means that the emissions during their production occur in these countries. We therefore think that it is required to study the issue at an international level.

There is no comprehensive information about the forms in which nanomaterials in textiles are present in the market. To provide transparency about the products and their ingredients for the players in the value-added chain and for consumers, textiles containing nanomaterials should be notified to a registry for nanomaterial-containing products for which the release of nanomaterials across their entire life cycle cannot be ruled out.

Consumers should be informed about potential environmental benefits and potential environmental risks of textiles equipped with nanomaterials.

Designers, manufacturers and consumers should in particular review the use of precious metals and rare materials in textiles for their purpose and intended function. While the use of nanosilver can be useful in textiles of medical purpose, it may be a waste of valuable resources and pose environmental and health risks in clothes for everyday wear.

Researchers, product designers, consumers, and decision makers should continue to share information, last but not least to protect the environment.

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