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Summary

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Nanoparticle emission of selected products during their life cycle

Summary

by

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1. Background

Nanoparticles[1] are used in many areas and products because of their properties and it is expected that the use of nanoparticles in products and applications will increase in future and so will their exposure to man and to the environment. (e.g. Nowak & Bucheli 2007). The present knowledge about the release scenarios, transportation and properties, retention and effects of nanoparticles in their life cycle is sketchy. In the course of this study, possible exposure and release paths of nanoparticles from products will be summarized based on data from literature and indications about the behaviour of these particles in different media is given. The complete product life cycle of various materials will be considered (Production, application, disposal, with possible exposure paths, as well as the retention and properties – the deagglomeration, agglomeration, retention time, ability to dissolve in water, reaction with other materials). Besides assessing the exposure, available measurement standards and methods will be analysed for their suitability in evaluating nano-materials and nano-objects.

Specification of the object of study

Nanoparticles are employed in a variety of products in different forms and functions. In the course of this study, the following materials were chosen in accordance with the client:

- Nanosilver – currently the most used nanoparticle (Woodrow Wilson Database 2009).
- Titanium dioxide – used in a variety of products
- Carbon Black – has been used for a long time in many products
- Cerium oxide – naturally occurring from burning processes.

For every material a commercially available product was chosen (in accordance) for which a release of nanoparticles in the course of its life cycle can be expected.

[1] This report uses the definition of the term as stated in the ISO Technical Committee 299.

- Nanosilver – Wiping cloth
- Titanium dioxide – Wall paint
- Carbon Black – Bulking agent in tires
- Cerium oxide – Additives in Fuel (Diesel).

2. Exposure

Due to the increasing use of nano-materials in products, there is also an increased risk of possible exposure to humans and to the environment. Humans can thereby be set out to different exposure scenarios and intake paths via the environment. There are different phases in the life cycle of products whereby nano-objects or nano-materials could be released: during production, during application or during disposal (burning, depositing, recycling). Release can take place in different environmental compartments such as air, water and soils, where the nano-objects or nano-materials are exposed to different abiotic and biotic circumstances which again could influence the retention and properties of the released substances. Nano-objects could therefore not only be released as single particles rather also as particles embedded in a matrix, which may also affect its properties (e.g mobility). Since many nano-objects are functionalized, the release of such nano-objects is also possible (Nowack & Bucheli 2007). Functionalised nano-objects depending on their functionalisation, can behave differently in the environment (e.g. reduction in agglomeration) than non-functionalised nano-objects. The surfaces of nano-objects can also be modified by the accumulation of organic material or the agglomeration and deagglomeration of these nano-objects can be influenced by humine (Hyung et al. 2007, Domingos et al. 2009). Furthermore, due to the high mobility of nano-objects, they could be used as carriers for other substances. (Moore & Willows 1998, Xia et al. 2004, Zhang et al. 2004). The release of nano-objects from products in the environment and their properties can therefore be very different depending on the product as well as the abiotic and biotic conditions in the environment.

3. Particle measurement techniques

Some difficulties faced when dealing with measurement techniques for assessing nano-materials are the small size of the particles, their different properties and measuring very small concentrations in compartments where a high concentration of naturally occurring nanoscale particles exist (Klaine et al. 2008, Burleson et al. 2004). For particles that commonly exist in natural systems, e.g. iron-nanopaticles, it is currently not possible to distinguish between these particles which are naturally present from the particles which are artificially introduced into the system (Kuhlbusch et al. 2008b). One way of experimentally detecting nano-objects particularly in fixed matrices like soil, is to disguise these particles (e.g. through radioactive and fluorescent methods) or to produce them with a particular surface consistency (Tiede et al. 2008).

Different measurement techniques exist in the area of fine particle research or colloidal chemistry, which are currently being tested for their suitability for detecting nanoscale material. Generally, methods for determining particle size distribution e.g. Scanning Mobility Particle Sizer (SMPS, airborne) or Dynamic Light Scattering (DLS, aquatic media) are the most commonly used methods because they provide a particle size-based concentration. These methods are not always applicable or rather do not always provide accurate results under all conditions.

4. Materials

4.1 Nanosilver

The products which are considered in the course of this study have surface bound nanoscale silver in order to enable the release of silver ions. The more toxic form of silver is probably silver ions which are mainly released when it comes into contact with water from the considered products. Because of the larger surface area to volume ratio for nanoscale silver, it is expected that silver ions are released faster per unit mass of nanosilver. Furthermore it is discussed that, nanoscale silver particles could possibly penetrate into cells and thereby lead to an increase in the concentration of silver ions which may then have a toxic effect on the cells. The release and exposure to silver ions is expected due to the antibacterial nature of the products, since this only occurs when the silver (in the form of nanoscale silver or silver ions) interacts with the environment. Benn & Westerhoff (2008) showed in their study the release of silver ions as well as nanoscale silver from textiles (socks) so that the exposure of nanoscale silver to humans and to the environment can be expected.

A quantitative characterisation of the release of nanoscale silver and as silver ions from a particular phase of washing wiping cloth, cannot be realised due to insufficient data.

Mechanical processes which release nanoscale silver in air from textiles and coatings are of little interest for the products considered here (Blaser et al. 2008). It has not yet been examined if the emission and exposure paths during the production of these products are relevant.

4.2 Titanium dioxide

During production, by carefully following particular guidelines, there is no significant release of TiO_2-nanoparticles in the atmosphere (Kuhlbusch et al. 2009). It has not yet been investigated if nanoscale TiO_2 or nanostructured TiO_2 material is released when cleaning the production equipment. During the application of products which contain nanoscale TiO_2 as photocatalytic substances in coatings, the release of nanoscale TiO_2 was established. (Kaegi et al., 2008; Hsu & Chein, 2007). Following a study from Kiser et al. (2009) it could be shown that during the cleansing of the drainage of a sewage plant, a small amount of the registered TiO_2 was not retained in the sewage sludge but rather could make it through the sewage plant into surface waters. It would have to be investigated in a separate research if nano-ojects, nano-structured materials or TiO_2.embedded in a matrix are released when sewage sludge is disposed of or introduced into soils.

An exposure of the considered products to the environment likely occurs primarily in the aquatic phase, due to the method of application of these products. Besides the aquatic dispersal paths, direct exposure to humans also occurs during the use of cosmetic products which contain nanoscale TiO_2. Initial studies which deal with the dermal uptake of nanoparticles, showed no increased risk for healthy skin (Nanoderm Final Report). Workers who process products containing nanoscale TiO_2 such as wall paint, are dermally exposed to these particles as well as through respiration and orally. The level of this exposure as well as a risk assessment for the workers has not yet been investigated.

4.3 Carbon black

Contact with unbound (uncombined) carbon black can be expected particularly during production. A study of the release of carbon black during industrial filling has shown that during the filling process, no significant amount of nanoscale carbon black particles are released (Kuhlbusch et al 2004 & 2006). During application of nanoscale carbon black as a bulking agent in tires, it could be shown that during abrasion, besides particles in the micrometer size range, ultra fine particles are released (Thorpe & Harrison 2008, Dahl et al. 2005, Fauser 1999). It is not clear if these released particles are actually primary carbon black particles or secondary carbon particles which are formed during nucleation. The amount of particles which are released is also unclear. Studies about the release of carbon black during disposal are not known to the authors.

Carbon black can be taken in through respiration, by swallowing or through the skin. Due to the application areas, release can primarily be expected in air. Humans are therefore principally exposed to nanoscale carbon black through respiration. Results from the Nanoderm final report show that an uptake through the skin is unlikely. It can be assumed that animals are also primarily exposed to nanoscale carbon black through respiration. It is still unclear if a dermal and oral uptake in animals is relevant. It is conceivable that through sedimentation or through a washout, nanoscale carbon black from air can get into the soil or into surface waters. The discharge of “natural carbon” through nanoscale carbon black seems to play a negligible role because of the high level of background concentration caused by burning soot in natural compartments (Koelmanns et al. 2008).

4.4 Cerium oxide

Cerium oxide is mainly used as catalysers (e.g. diesel fuels), as polishing agents, in coatings in IR- and UV-filters and as electrolytes in fuel cells (Asati et al. 2009). Recently, it was shown that nanoscale cerium oxide can be used as an antioxidant as well as against radiation damages, oxidative stress and inflammations (Asati et al. 2009). The authors are unaware of any information about the release of nanoscale cerium oxide during production. By using nanoscale cerium oxide as additives in fuels, release in air as well as in water and soils through spilling, is possible. Release in the atmosphere when used as additives has been established in various studies (Park et al. 2008, Jung et al. 2005, Farfaletti et al. 2005).

The study of Limbach et al. (2008) deals with the retention and removal of oxidised nanoparticles (including cerium oxide) from model sewage plants. This study shows that not 100 % of the input nanoscale cerium oxides are retained by the sewage plant. A small amount (about 2 – 5 ppm of the original 100 ppm) can make it through the sewage plant and get into surface waters, whereby a stabilizing effect on the cerium oxide nanoparticles through the components of the sewage was noticed. Domingos et al. (2008) saw similar results and showed that humic acids could have a stabilizing effect on nanoparticles. If the sewage sludge is applied to soils, nanoscale cerium oxide particles and cerium oxide particles which are embedded in matrices, are released and get into the soils during the decomposition of the sewage sludge (depending on the type and amount of organic carbon in the sewage sludge). This must however be confirmed by further studies.

Humans are therefore primarily exposed to nanoscale cerium oxide through respiration. It can also be assumed that animals are also principally exposed to nanoscale cerium oxide through respiration. It still has to be shown if a dermal or oral exposure in animals is relevant. Due to the very small pool of data, more research is needed to make a profound statement about the exposure to humans and the environment.

5. Conclusion

Emission of nano-objects and nano-structured material from products depends on different factors (e.g. type, shape, function, application). When nano-objects are released from products, they usually don’t exist as loose nano-objects, rather, they could be embedded in a matrix, could be functionalized or coated which in turn affects their properties. When the particles are released in the environment, they are also exposed to various abiotic and biotic factors which could affect their properties. The release and the behaviour of particles in the environment could therefore differ greatly from product to product and also depending on the abiotic and biotic factors they are exposed to. With the current state of knowledge, no particular substance groups or mechanisms for release, transportation and retention in the environment can therefore be formed.

There are several studies which give indications about the processes concerning the properties and retention of nanoscale particles in air. There are also initial studies which give some indications about the properties and retention of nano-objects in water and soils. These are however difficult to quantify with the current state of measurement techniques.

This heterogeneous picture of the release and transport of particles is also shown for the substances and products examined in this study. The main release paths in the course of the life cycle occurs in air or water, whereby nanoscale TiO_2 and silver are most probably released primarily in water while carbon black and cerium oxide are released primarily in air.

A direct exposure to humans and animals can occur through the skin, orally or through respiration. Dermal exposure however plays a minor role for humans. It is unclear how relevant the dermal exposure is for other organisms. A direct oral uptake seems unlikely for adults. The relevance of an indirect uptake through foodstuffs still needs to be studied. For other organisms, particularly aquatic organisms, there seems to be more relevance in oral uptake.

The respiratory intake is seen by many scientists as the most important uptake pathway in humans. In the products considered in this study, model estimates show that the environmental concentration of the examined nano-objects is currently not critical, whereby it is expected that in future the concentration of substances such as nanoscale TiO_2 can reach critical levels. There are knowledge gaps in the area of exposure concentrations especially concerning possible bioaccumulation of nanoscale materials.

Generally, the reference study presented here shows that the current state of knowledge in the area of release, transportation, retention and exposure of nano-objects to humans relies on a few studies. The current knowledge is insufficient for making any generalised statements which are relevant for risk assessment. For some cases no easy applicable techniques (e.g. detection of nanoparticles in soils), standards (e.g. quantification of release scenarios), process information (e.g. agglomeration / deagglomeration) are available allowing to derive the necessary broader understanding.

From the results of the study, the following research needs and need for action arise:

- Quantitative examination of the release of particles from products during their life cycles, including the characterization of the shape / functionalisation where the nano-objects / nano-materials are release, for different and also standardised conditions.
- Qualitative and quantitative examination of the interaction of nano-materials with water and soils

- Linking of the experimental examinations with the modelling of the release, proliferation/mobility and expected environmental concentration
- Development of measurement techniques specifically for nano-objects in aquatic media, sediments and soils.