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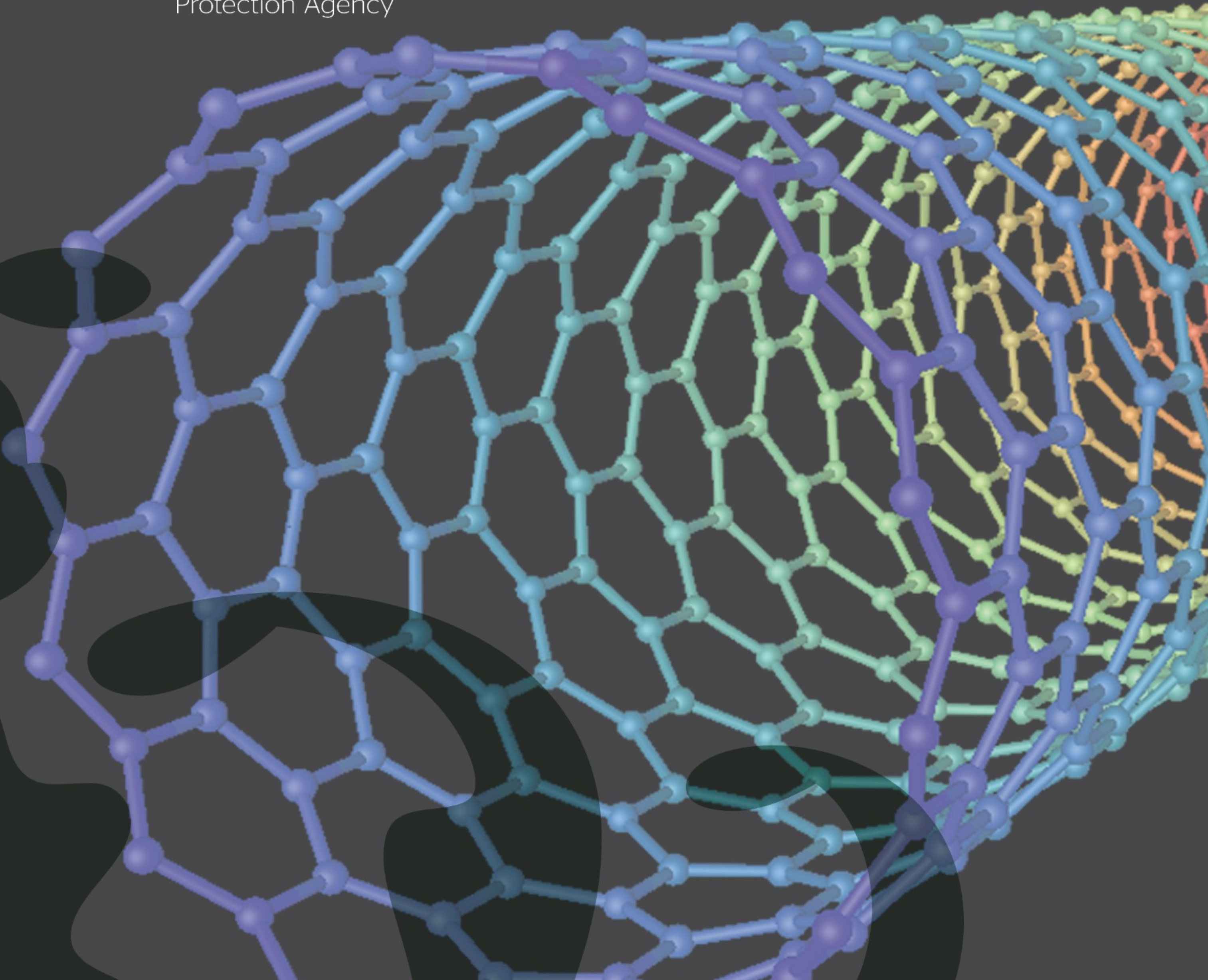

Better control of nanomaterials

- summary of the 4-year Danish initiative on nanomaterials

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Better control of nano
- summary of the 4-year Danish initiative on nanomaterials

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Content

Preface

An initiative on nanomaterials and their safety, to be carried out between 2012 and 2015 was included in the 2012 Budget prepared by the Social Democrat led coalition government in agreement with the Red-Green Alliance.

In the national budget agreement the initiative is described as follows (unofficial translation):

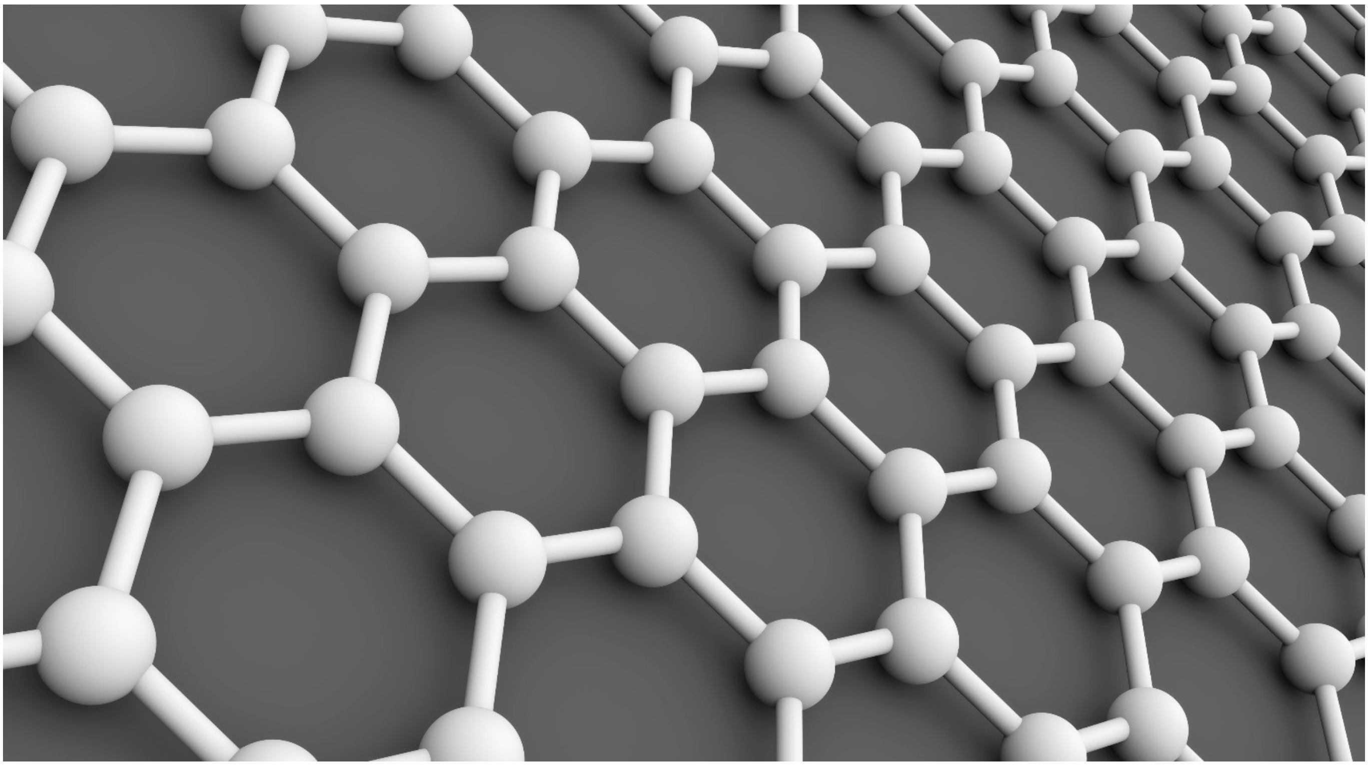
"Better control of nanomaterials and their safety.

The quantities of nanomaterials that are produced and used, are unknown. The levels of these materials, to which consumers and the environment are currently exposed, are therefore also unknown. In addition to this, there are some crucial points on which knowledge of the possible harmful effects on consumers and on the environment exposed to nanomaterials, is missing.

The Government and the Red-Green Alliance commit to creating greater clarity on the pathways of exposure to nanomaterials and the consequences for consumers and the environment. Six million Danish kroner have been set aside annually to strengthen these efforts. Current work by both the Danish Centre for NanoSafety and the Environmental Protection Agency will be coordinated. Increased efforts in the field of nanotechnology include the development of a nano product database in cooperation with other countries. The possibility of giving institutions and businesses a "Duty to Report" will be investigated."

This report presents the overall results of this work. The results include a total of 30 reports and the establishment of a register of nano-products.

The original report is in Danish and this is the English translation.



Summary

Nanomaterials comprise very small objects or particles. Their use opens up new technological possibilities, but also new environmental and health concerns. The "Better control of nanomaterials" initiative over the past four years has aimed at creating an overview of the possible risks of using nanomaterials.

The work focused on Danish consumers and the Danish environment and the outcome is described in 30 reports. The initiative also led to the establishment of the Danish nano product register (Statutory Order 644/2014).

The "Better control of nanomaterials" initiative included a number of surveys of where nanomaterials are used in consumer products.

In parallel with this work, the Danish NanoSafety Centre at the National Research Centre for the Working Environment completed a four-year initiative that focused on nanomaterials in the working environment. Therefore, the "Better control of nanomaterials" initiative does not address the working environment but has been coordinated with the Danish NanoSafety Centre.

Generally, there is still a need for more information on where nanomaterials are used, on which nanomaterials that are used and on the extent to which consumers and the environment are exposed to them.

Work is also in progress to facilitate a continuous improvement in knowledge that will allow better assessment of the hazards of nanomaterials and the health and environmental risks that they pose.

The conclusions of this summary report should therefore be taken with some reservation. These reservations are further elaborated in the individual reports from the initiative.

Nanomaterials in consumer products often occur in a so-called solid matrix from which they would normally be released very slowly and therefore, it is considered not likely that they pose risks to the consumer.

Nanomaterials are also used in a number of liquid and powder products. The results of the "Better control of nanomaterials" initiative show that consumers when using these products often have skin contact with them. Damage to the skin or absorption of nanomaterials through the skin however, is very limited.

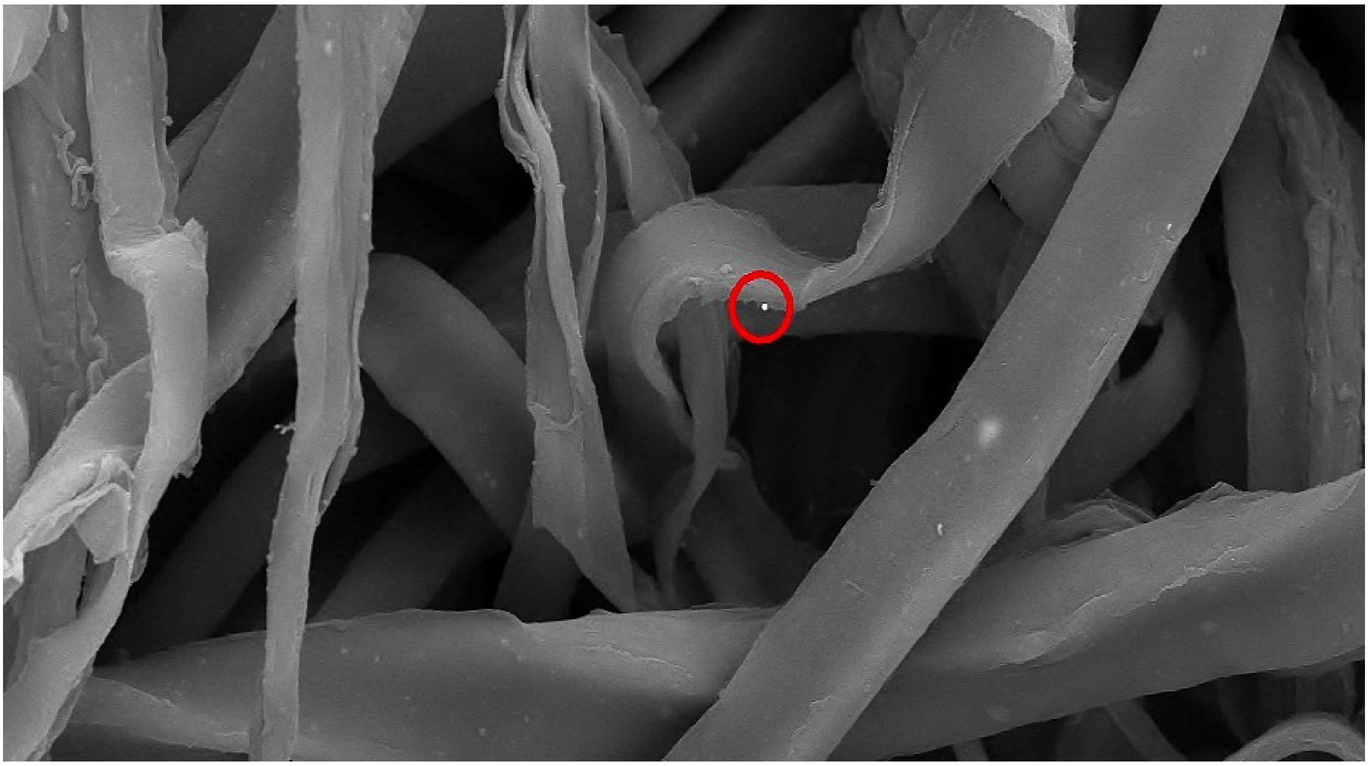
On the other hand, the results show that there could be risks to the consumer from applications which may result in the inhalation of nanomaterials. This, for example, applies to spray painting using a spray gun without proper protective equipment, an activity that would be hazardous even if no nanomaterials were present in the paint. It is also considered likely that there may be a risk when sanding surfaces that have been treated with specific types of product in which the nanomaterial is not bound in a matrix on the painted surface. Thus, this does not apply to all painted surfaces in general. In a variety of other consumer applications, it is anticipated that there is a possible risk associated with the use of some spray and powder products. A possible risk is also present when some solid products are treated mechanically causing generation of dust. It should be emphasized that the projects forming part of the "Better control of nanomaterials" initiative generally adopt a very cautious approach, because knowledge on exposure and effects remains limited. For example, a relatively high content of nanomaterials was assumed to be present in products and "worst case" assumptions were made for releases and the possible exposure of consumers.

This may be the reason why one of the studies does not exclude the possible effects of ingesting two types of nanomaterials that are used in food additives. Note that these food additives are under review at EU level. The same study indicates, based on conservative worst-case assumptions, that nanomaterials in sunscreen products may be ingested (one example is sun protecting lip balm) and that this can be linked with a possible risk. The report stresses, however, that on the basis of current knowledge, there is no risk associated with the uptake of nanomaterials through the skin. The report highlights the benefits of using sunscreen and that these benefits need to be compared to the possible risks associated with exposure by ingestion.

The initiative suggests that there is no significant risk to the freshwater environment from current usage of nanomaterials and their potential for release to the environment. Calculations indicate that there may be a local risk from some nanomaterials in areas located immediately adjacent to the discharges from wastewater treatment plants. Due to lack of information, risks to the marine environment, sediment and soil were not assessed. There is still a great need for new knowledge about the prevalence and effects of nanomaterials in the environment. In addition, an increase in the use and the resulting increase in releases to the environment, of materials such as carbon nanotubes can be a potential risk to the environment.

The European Commission states that existing legislation applies to nanomaterials. There is a growing recognition, however, that information required by current legislation is insufficient to address the specific properties of nanomaterials. In addition, in some cases more information is desired on where nanomaterials are used. At EU level, the need to adjust the requirements for information and assessment of nanomaterials in the general chemicals legislation (REACH), is being examined. Additionally, a number of sector specific laws have already been adapted or are in the process of being adapted to require labelling, reporting and / or specific assessment of products containing nanomaterials. Discussions have been taking place for a number of years at EU level to investigate the possibilities and consequences of creating a European register of nanomaterials. Meanwhile, a number of EU countries are considering, or have already implemented national registers, among these is Denmark.

Industry and industry organisations call for a solution at EU level, but express general satisfaction with the process of creation of the Danish register and the information and guidance that supported its implementation. Initial experience from the first entries into the Danish register, however, seems to indicate that despite these efforts, it is difficult for many Danish companies to deal with nanomaterials and that it is difficult to obtain the necessary information from the manufacturers and supplies who are typically located abroad.



1. Introduction

New applications of nanomaterials and environmental and health concerns led the government in 2012 and its partners to allocate a total of 24 million Danish kroner in the budget to address these concerns. The allocation was intended to clarify the exposure pathways for nanomaterials and the possible harmful consequences.

The initiative, known as "Better control of nanomaterials", was intended to achieve better clarity on exposure pathways and the consequences of using nanomaterials to consumers and the environment. The initiative also included the development of a nano product register with associated legislation.

This report presents the results of the "Better control of nanomaterials" initiative and briefly puts the work into perspective in relation to other activities taking place in the area of nanomaterials including research, surveys, standardisation and legislation.

This report describes the overall conclusions, whilst the detailed results of the initiative can be found in the 30 reports from the initiative [1-30], which should be consulted to understand the full context of the topics analysed. This also applies to assumptions and uncertainties related to the assessment of the prevalence of nanomaterials and their effects.

New opportunities using nanomaterials

Nanomaterials create opportunities for new and improved products and processes. For example, lightweight, strong materials can be produced and also products with improved electrical and optical properties. Nanomaterials can for example, also be used to produce products with smooth, strong surfaces reducing frictional resistance and allowing more effective cleaning. Another very important characteristic of nanomaterials is their small size. This gives them a greater reactive surface area compared to the same mass of material with larger particle size. This increased reactivity per mass of material is useful in a wide range of products and chemical processes. It allows faster processes and in many cases, smaller amounts of material are needed, compared to conventional solutions. One of the projects under the "Better control of nanomaterials" initiative, specifically sought to highlight how the properties of nanomaterials are exploited or have been considered in products and technologies that aim to solve environmental challenges. This can include the remediation of polluted soil, water or air, improving hygiene in the health care sector and a variety of applications aimed at energy conservation and energy optimisation [28].

Concerns for the environment and health

Some of the characteristics that are useful in producing new and improved products also give cause for concern. Some nanomaterials are entirely new types of materials, which may have new and unexpected effects on living organisms.

The small size of nanomaterials leads to concern about whether they can cross biological membranes and thus be taken up by cells and organs. In addition, small particles may accumulate deep in the lungs if inhaled, and remain there for a long period, because they are cleared slowly from this part of the lung. There is also a concern that the increased reactivity of known materials in nanoform could lead to increased or unwanted effects in humans and the environment.

Sustainable use - advantages and drawbacks

An important aspect of the sustainable use of nanomaterials is to exploit their properties, without creating unnecessary risks in terms of undesirable effects on humans and the environment.

Another important question is whether nanomaterials are a good idea from an overall environmental perspective. Life cycle assessment (LCA) is a recognised method / tool for examining such questions. LCA examines all stages of the product life cycle and all types of impact on the environmental. Whilst the use of a product may be associated with environmental benefits (e.g. energy savings), we know that it is very energy intensive to produce certain types of nanomaterial and that some nanomaterials contain rare metals that may be scarce resources.

The "Better control of nanomaterials" initiative has not had as its main focus, the carrying out of life cycle assessments. The project on nano products in environmental technology revealed however, that so far, relatively few such assessments have been completed, although there is general agreement on the wisdom of carrying them out [28].

Example: Carbon nanotubes (CNT)

One of the "Better control of nanomaterials" initiative projects addressed carbon nanotubes [30], an example of a new nanomaterial. Carbon nanotubes are hollow tubes made up entirely of carbon. Carbon nanotubes are long and strong and may be electrically conductive. They have many potential uses such as reinforcement in composite materials and in sensors and light emitting diodes (LEDs). Carbon nanotubes resemble asbestos in that they comprise long, thin and insoluble fibres. A number of toxicological studies have been carried out on the hazardous properties of carbon nanotubes focusing on inhalation hazards.

Studies on animals have shown that carbon nanotubes that are inhaled, trigger a protracted inflammation and other biological defence mechanisms known as acute phase response, at doses that are far below the limit values for dust or carbon black (which like carbon nanotubes are chemically composed of carbon). Prolonged acute phase response leads to an increased risk of cardiovascular disease. Exposure to a particular type of carbon nanotube is shown in two different toxicological tests to lead to cancer. Exposure to a different type of carbon nanotube did not cause cancer. Inhalation of carbon nanotubes can therefore increase the risk of both cancer and cardiovascular disease.

Based on these findings, the US National Institute for Occupational Safety and Health and researchers at the EU Joint Research Centre both suggested a threshold limit value (TLV) for the working environment of 0.001 mg/m^3. This TLV is more than 1000 times lower than the equivalent value for carbon black (3.5 mg/m^3). The proposed limit value for the external environment was even lower at 0.00025 mg/m3.

Regulation of nanomaterials

Nanomaterials are used in a variety of contexts, and many believe that their use will increase explosively over the coming years [21]. This has led to increased political focus due to the environmental and health concerns associated with nanomaterials. At EU level, the European Commission has stated that the laws regulating chemicals also apply to nanomaterials as the term *nano* simply refers to a different size (nanoform) of a given chemical [32, 33, 34]. This applies both to the general chemicals legislation (REACH) and legislation that covers specific product groups of chemicals such as pesticides and biocides.

It is recognised however, that this legislation does not adequately address specific properties of nanomaterials. There is a widespread political desire for products that actually contain nanomaterials to be identifiable. Chapter 6 describes how a number of rules are already in place or are about to be changed in order to address this issue.

The chapter also explains that activities are underway to clarify whether to establish a register at EU Level, in order to provide greater clarity on how nanomaterials are actually used. This work takes time, and has caused a number of countries to set up national registers. The creation of the Danish nano product register should be seen in the context of this process. The European Commission has proposed a definition of nanomaterials. This is discussed in more detail in the next chapter. EU member states and institutions are asked to apply this definition in political and legislative activities [35]. The Statutory Order on the Danish nano product register (644/2014) makes use of this definition.

The purpose of the "Better control of nanomaterials" initiative

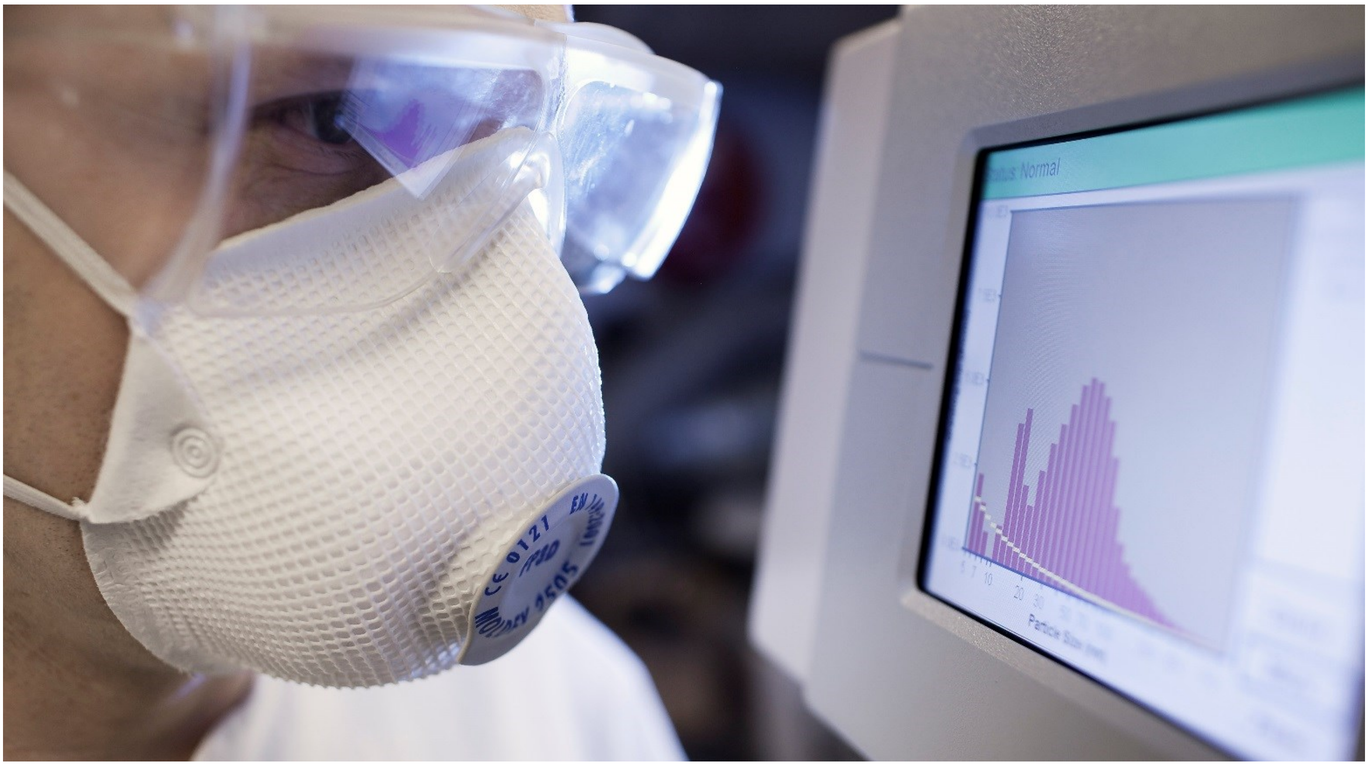
The overall objective of the "Better control of nanomaterials" is described in the 2012 National Budget agreement (unofficial translation): " *The quantities of nanomaterials that are produced and used, are unknown. The levels of these materials, to which consumers and the environment are currently exposed, are therefore also unknown. In addition to this, there are some crucial points on which knowledge of the possible harmful effects on consumers and on the environment exposed to nanomaterials, is missing. The Government and the Red-Green Alliance party commit to creating greater clarity on the pathways of exposure to nanomaterials and the consequences for consumers and the environment. Six million Danish kroner have been set aside annually to strengthen these efforts. Current work by both the Danish Centre for NanoSafety and the Environmental Protection Agency will be coordinated. Increased efforts in the field of nanotechnology include the development of a nano product database in cooperation with other countries. The possibility of giving institutions and businesses a "Duty to Report" will be investigated."*

Readers guide

Chapter 2 of this report provides a brief introduction to what nanomaterials are, why they are used, and to the challenges that exist in determining the presence of nanomaterials in products and what these challenges mean for the regulatory framework in this field. Chapter 3 focuses on the presence of nanomaterials in consumer products. The chapter can be read as an introduction to the two subsequent chapters that focus in more detail on the health risks to consumers and on the risks to organisms in the environment.

Chapter 4 covers the health related risk to consumers. It summarizes the results of one major study of consumer products in general and a number of specific studies that focus on risks associated with specific product groups. The following chapter (Chapter 5) summarizes the knowledge of the possible effects to the environment that are identified in the "Better control of nanomaterials" initiative. Current techniques cannot measure nanoparticles in the environment or in discharges to the environment. A sophisticated model has therefore been developed to estimate potential concentrations in the environment to be compared with existing knowledge on the effects of nanomaterials. This enables the risk to be assessed.

Chapter 6 completes the report with a brief description of the legislation in this area and puts into perspective, the initiative and the Danish nano product register in relation to other activities within the EU. The chapter also describes the experience gained from the first data registrations into the nano product register.



2. What are nanomaterials?

The definition of nanomaterials proposed by the European Commission is used in the Danish Statutory Order among other places. There are however, challenges in determining whether individual products contain and release nanomaterials.

The meaning of "nano"

"Kilo" means thousand (1000) and one kilometre is another way of writing the 1000 meters. By the same convention, "nano" means one billionth (0.000000001 or 10^{-9}), and a nanometre (nm) is another way of writing one billionth of a meter.

Nano size typically refers to the range of 1-100 nm. This range, is included in most definitions of nanomaterials. In Europe the most common definition of nanomaterials is that recommended by the European Commission [35], and ISOs definitions of a wide range of nano terminology [36].

Definitions of nanomaterials

Although ISO and the European Commission agree that "nano" in this context refers to the size range 1-100 nm, they differ in a number of other areas.

The ISO definition of nanomaterials include both individual nano-objects such as particles and so-called nanostructured materials. The latter refers to materials which may have internal nanostructures such as nano-sized pores and / or a surface with nano-sized structures. The EU definition refers only to particles understood as "*a minute piece of matter with defined physical boundaries*" [35]. This difference is due to the fact that the ISO definitions are most often used in a technical / scientific context, whilst the EU definition is used in a political and regulatory context focusing on how people and the environment might become exposed to nanoparticles. The internal nanostructure of stainless steel for example, would not be relevant in a regulatory context. However, it is important to stress that in its preamble, the EU definition states that it refers to particle size alone and not to the potential harm that the particles might cause.

Another major difference is that the ISO definition refers to the individual piece of matter, such as a single nano object whilst the EU definition refers to the entire material, for example, a powder which comprises many nano particles. Such a powder rarely consists of completely identical particles but is typically a mixture of different particle sizes which form a size distribution. Such a powder is according to the EU definition

Nano comes from nanos, meaning dwarf in Greek. One nanometre (nm) is one billionth (10^{-9}) of a meter and one thousandth of a micro-meter.

Nano-sizes typically refer to objects with a size range of 1-100 nm.

A human hair is about 50,000 nm thick.

The wavelength of visible light is 400-700 nm. Particles smaller than this interact differently with visible light than larger particles.

Nanoparticles are so small that they cannot be seen with an ordinary optical microscope.

defined as a nanomaterial if more than 50% of the unbound particles (primary particles) are between 1 and 100 nm. This implies that using the EU definition, a powder would not necessarily be defined as a nanomaterial, even though it contains nano-sized particles. On the other hand, a material whose mass comprises mainly particles larger than 100 nm, would still be a nanomaterial if the lighter, smaller particles between 1 and 100 nm comprise more than 50% by number.

Nano Concepts

The definition of nanomaterial [35] recommended by the European Commission has been followed in the Danish Statutory Order on a nano product register. A number of concepts from the EU definition, used in the characterization of nanomaterials are explained here:

'**Nanomaterial'** means a natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50 % or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm-100 nm.

'**particle'** means a minute piece of matter with defined physical boundaries.

'**aggregate'** means a particle comprising of strongly bound or fused particles.

'**agglomerate'** means a collection of weakly bound particles or aggregates where the resulting external surface area is similar to the sum of the surface areas of the individual components.

"Unbound particles" (or 'primary particles') - Particles that are not bound in an aggregate or agglomerate. NB! Based on point (12) of the preamble to the EU definition [35].

Nanomaterials – naturally occurring, incidental or manufactured materials?

The EU definition basically covers all types of nanomaterials, including: i) nanomaterials formed by natural process such as volcanic eruptions, ii) nanomaterials formed unintentionally by human activity such as the use of wax candles or the burning of fossil fuels and iii) intentionally manufactured nanomaterials.

In a given context chemicals legislation is typically aimed at addressing manufactured materials and chemicals. This does not of course prevent the EU definition being applied to assessing whether these intentionally manufactured materials fall under the definition of nanomaterials or not.

It also needs to be stressed that the "Better control of nanomaterials" initiative focuses on manufactured nanomaterials and in particular those used in consumer products. One of the underlying reports however, investigated nanoparticles that consumers could be exposed to from other sources [18]. These results are used to put into perspective, the manufactured nanomaterials that consumers are exposed to as opposed to nanomaterials from other sources. This is discussed further in Chapter 4.

How do nanomaterials work?

Particles or structures that are very small can exhibit specific physical properties that the same substance or material does not have when present in the form of larger particles or structures. This is exploited in some nanomaterials, whilst other applications simply exploit the fact that the total surface area is very large.

Large surface: Nanomaterials often comprise well known chemicals. A number of metals and metallic compounds such as silver, copper, copper carbonate and zinc oxide can release metal ions from their surface. These have antibacterial properties. Reducing the particle size of these materials, increases the reactive surface area, so that the nanoform of these materials is a more efficient antibacterial agent than the same material in the form of larger particles.

Transparency: Since nanoparticles are very small compared to the wavelength of visible light, they do not reflect light the same way as larger particles. An example in which this property is utilised is sun protection products using the white pigment titanium dioxide. Titanium dioxide has UV-absorbing properties. Previously, the pigment used in sunscreens made them appear white. Today, sun protection products use the nano titanium dioxide form resulting in a transparent product. Similar effects can be achieved using the white pigment nano zinc oxide and nano cerium oxide, whilst transparent coloured paints and plastics are produced using nano-sized colour pigments [15].

Photocatalytic effect: Titanium dioxide occurs in different crystalline forms. In particular, the anatase crystal form is photo-catalytically active. This means that, in the simultaneous presence of light and moisture, so-called free radicals are released and these have an antimicrobial effect. This feature is enhanced by the use of titanium dioxide in nanoform. The antimicrobial effect of nano titanium dioxide is utilised to an increasing extent for many different purposes, and it is potentially useful in the health sector [28].

Special physical and electrical properties: Nanomaterials include, both known materials in nanoform and new nanomaterials. Probably the technically most interesting new materials are based on carbon in the form of graphene, carbon nanotubes, or spherical carbon structures (fullerenes). Graphene consists of flakes with a thickness of just a single or few layers of carbon atoms. Carbon nanotubes consist of single walled graphene cylinders or concentric cylinders (multi-walled). As discussed in the example in Chapter 1, the electronic and structural properties are used in a wide range of products. The same applies to a number of other carbon-based nanomaterials. These new materials are different from previously known materials, and their special properties mean that there is extra vigilance surrounding any possible unexpected effects that they may have on organisms.

Optical quantum effects: So-called quantum dots utilise special optical quantum effects that can occur in materials in the nanoform. Attempts to utilise these effects have been made in connection with LED light bulbs and optical instruments.

Forms and modifications

Nanomaterials are often understood as being very small round particles. This however, is far from always the case. Depending on the application and the manufacturing technique, nanomaterials may also be needle-shaped, rod shaped, rhomboid, fibres, etc.

Nanomaterials can also be so called "nanocarriers" that can transport another substance. Considerable attention is focused on such "carriers" as among other applications, they show promise for the development of methodologies that deliver medication to the correct location in the body.

Nanomaterials are often referred to as if they comprise a single chemical compound. This is far from always the case. Many manufactured nanomaterials are covered with a thin layer of coating and / or are functionalised, meaning that there are other substances bound to the surface. Such modifications are often made to improve the properties of the nanomaterials. For example, nano titanium dioxide used in sunscreen products is surface-modified such that the free oxygen radicals formed by photo-catalysis, are trapped in the surface before they can cause damage to the skin. Nano-carriers for medicines can be surface treated to release the medication that they contain when the surface treatment recognises the organ or the cells that are to be medicated.

The word *nano* followed by the name of a chemical does therefore not necessarily describe the material uniquely. It is usual therefore, to speak of *characterisation* of a nanomaterial in terms of its chemistry, size, shape, surface modification, etc.

The above illustrates that there is almost infinite variety in the manufacture and design of nanomaterials. This is exploited commercially, but also poses challenges for the assessment and regulation of nanomaterials. In practice it would be difficult to investigate the hazardous properties of all specific types of nanomaterial. A major challenge in this context is whether data on the hazardous properties of a nanomaterial can be reused. For example, can information on a particular size of nano titanium dioxide with a particular surface modification, be used to assess the hazards and risks associated nano titanium dioxide of a different size and with a different surface modification?

Analytical challenges associated with nanomaterials

Because of the small size of nanomaterials and their tendency to clump together as aggregates and agglomerates there can be a number of analytical challenges in determining:

- whether the material falls within the EU definition of a nanomaterial.
- whether the nanomaterial occurs in the form of "free" particles, and whether nanomaterial included in a product is released from it.
- whether the nanomaterial is present in products or in the environment.
- whether, by testing the possible effects, the nanomaterial is present in the form of

primary particles, larger aggregates or agglomerates.

These challenges have been discussed in a number of the studies in the "Better control of nanomaterials" initiative. Several of the studies have focused particularly on these challenges [25, 27].

Challenges in relation to the definition of nano: There is not yet any standard specifying how the size of nanomaterials is to be determined in relation to the definition recommended by the European Commission. There are however, a number of activities underway to help alleviate this, among others the EU projects NANoREG and NanoDefine [31]. The recommended definition of nanomaterials is based on the size of the primary particles, but the materials are often present as larger aggregates and agglomerates, both when used to produce chemical mixtures and articles and in finished products. One of the projects under "Better control of nanomaterials" examined the use of pigments in nano size [15], and in this context, existing knowledge on the determination of pigments in relation to the nano definition was reviewed. Pigments are traditionally described in terms of "dynamic light scattering" and other methods that make use of an indirect determination to describe the size distribution on a volume basis. The European Commission definition however, refers to the number-size distribution, which cannot be determined using these methods, and in addition, it is not primary particles that are determined. It is possible to determine the size distribution of primary particles in pure nanomaterials quite precisely using transmission electron microscopy (TEM). This can rapidly become more difficult when the nanomaterials are in mixtures and articles. Various screening methods are therefore under consideration internationally including the use of the volume-specific surface area. At present, almost all pigments fall under the EU's proposed definition of a nanomaterial, since it is not possible to determine with any certainty, that they are not nanomaterials [15]. The same may well apply to many fillers for instance, used in paints and plastics and various other raw materials in powder form.

Challenges in relation to nano product register definitions: The Danish nano product register includes consumer products containing intentionally manufactured nanomaterials in which the nanomaterial itself may be released during normal use or use under conditions that can reasonably be expected. The "nanomaterial itself" refers to the nanomaterials added being released and that the released nanomaterial is not bound in a matrix. Since substances of any mixture will be bound to the surrounding molecules by weaker or stronger forces, it is not a simple matter to determine whether it is the nanomaterial "itself" that is being released. A study under the "Better control of nanomaterials " initiative has highlighted the issue via a literature review and a series of experiments [25].

The experiments investigated the extent to which the nanomaterial is released from shoe cream, crayons, cement and tiles whose surfaces had been treated with nanomaterials and releases from paint. The results indicate that the nanomaterials themselves are released or can potentially be released from all the tested products. The nanomaterials in liquid mixtures like paint and glue are bound by means of relatively weak chemical bonds and would typically be able to move quite freely in the mixture. The results also indicate that the nano particles in powder mixtures such as cement, are not strongly bound and will mainly be released as agglomerates. Nevertheless free individual particles can also be present in dust from the powder.

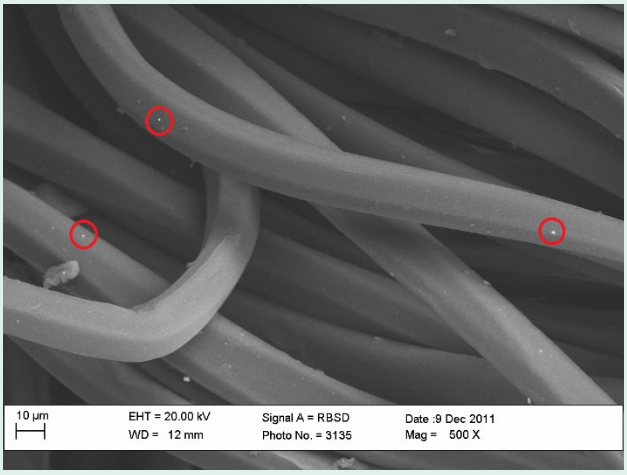
On the basis of the literature survey, it was also concluded that free nanomaterials would likely be released to the air in the spray application of liquids containing nanomaterials. As mentioned, it has proven difficult to obtain clear-cut results. In line with this, the current guidance for the nano product register specifies that nanomaterials in liquids shall be considered to be free and in principle, covered by the obligation to report.

Another related study focused on the possible release of nanoparticles from printer cartridges [14]. Measurements did not detect any release of nanomaterials from printer cartridges (neither laser cartridges nor inkjet cartridges) during printing. The study noted however, that other scientific publications had detected the release of the nanoparticles from the laser printers. During the refilling of inkjet cartridges, concentrations of nanoparticles were found that were far higher than the background level, and it was therefore concluded in the study that nanomaterials would be released during the normal expected use of refillable inkjet cartridges.

There are significant analytical challenges in determining the presence of nanomaterials in products and in determining in which form the nanomaterials are released by use of the products.

Example: Nanosilver (nano-Ag) in textiles

Silver is used as an antibacterial agent in many products. When the products are used, silver ions are released which act to inhibit microorganisms, and this mechanism is the same whether the silver is present in nanoform or in the form of larger particles. It is difficult to detect the nanomaterials in the finished products. A study of nano silver in textiles, in which the products were examined using scanning electron microscopy (SEM) found nanoparticles in only two of the 16 products tested [3]. The method did not have a sufficient spatial resolution to detect very small silver nanoparticles. The investigation was therefore followed up by a later study [24]. In 17 textile products, all of which contained silver, 11 samples containing silver particles were found. The particles however, all had cross sections of between 200 and 2,000 nm measured with an SEM method that should have been capable of measuring down to 5 nm. The SEM method was combined with EDX analysis, which can show whether particles down to a particle size of 20 nm are of silver. In six samples, which had a silver content above the limit of detection, silver particles were not detected. The samples could, in principle have contained silver particles, which were smaller than 5 nm. Production of silver particles smaller than 5 nm is not known, so the authors estimate that it is more likely that the measured silver was the background level in the fibres.



Scanning electron microscopy (SEM) of nanosilver particles marked by red circles on fibres from the inner sole of a sandal [3]

Although two studies were carried out, there is still some uncertainty about whether the products contain silver in nanoform even though nano particles could not be detected.

Determination of nanomaterials in products and in the environment: Nano particles are too small to be seen in an ordinary optical microscope, and therefore it is necessary to use techniques such as scanning electron microscopy (SEM) and transmission electron microscopy (TEM) to see them.

Scanning electron microscopy can produce an image which displays the three-dimensional structure a material or substrate in which the nanoparticles are lodged (see the nanosilver example above). Scanning electron microscopes however, seldom have a sufficient high spatial resolution, so that the particles often appear only as small dots and the smallest particles (close to 1 nm) cannot be seen at all. In addition to this, it is difficult to identify individual dots and impossible for the smallest particles. The technique therefore, is most useful when searching for particles of a known material. Higher resolution can be achieved using transmission electron microscopy (TEM) and the method as stated above, can be used in identifying and characterising a nanomaterial. It is more of a challenge however, to analyse articles and products in which nanomaterials may be positioned within a spatial structure. An example of this is nano silver on textile fibres (see example above). It is possible to determine the chemical composition of each particle by energy-dispersive x-ray spectroscopy (EDX). In a study of nano silver in textiles, an EDX technique made it possible to determine the material down to a particle size of about 20 nm [24].

It is however, still very difficult (and may not be possible) to count the number of particles of certain nanomaterials in composite matrices such as waste water or sediment samples.

A study that looks at how to formulate requirements for analytical methods for nanomaterials examines five cases that represent some significant issues, in which well-functioning analysis methods are important [27]. The results of the study have not yet been published.

3. Nanomaterials in consumer products

Several of the investigations forming part of the "Better control of nanomaterials initiative" have identified consumer products in which nanomaterials are used.

One can roughly divide the nanomaterials into two groups. In one group, the application intentionally exploits the nano properties of the materials used. In the second group, the materials fall within the definition of nanomaterials, but the applications does not intentionally make use of any special nano properties. One example of the latter is pigments. One study reaches the conclusion that virtually all pigments would fall within the EU definition of nano, but the nano properties are only exploited in a fraction of pigments consumed [15].

Identification of actual products in which nanomaterials are used, and obtaining an overview of their individual uses has been a challenge. Manufacturers of nanomaterials list a wide range of potential applications of the materials on their websites. Danish and foreign nano databases also list many examples of products that claim to contain nanomaterials.

In general however, it is difficult to identify specific products in Denmark containing nanomaterials where the nano properties are intentionally exploited. In the absence of information on the quantities of nanomaterials in products in Denmark, calculations of releases and evaluation of the environmental and health consequences have in many cases, been based on other information sources such as the consumption throughout Europe.

Nanomaterials that are used to intentionally exploit their nano properties, are apparently not manufactured in Denmark. Nanomaterials however, are used to a certain extent in the manufacture of various products which has been described in previous studies.

Nanomaterials in Consumer Products

Cosmetics: Nano-titanium dioxide applied as UV protectant in cosmetics is amongst the most well documented applications of nanomaterials. Other cosmetic applications include various pigments such as iron oxides, carbon black and aluminium hydroxide [7].

A study that focused on nanomaterials in cosmetics [26] was not yet complete when this report was published and the results can therefore not be described further.

In the future, more knowledge will be available on the content of nanomaterials in cosmetics as the new Cosmetics Regulation require nanomaterials to be reported. This is discussed further in Chapter 6.

Spray products: A survey of spray products on the Danish market examined 71 different spray products [19]. In addition to different types of spray paint containing pigments there were also spray products containing nano silica and nano titanium dioxide. These products are typically used for UV protection, antibacterial protection and impregnation. It was also concluded that there may be spray lubricant products containing nanomaterials based on molybdenum, silica and borate, since lubricant additives are marketed as containing these nanomaterials.

Some spray products are marketed as nano products but contain no nanomaterials. They do however, form nanostructures on the treated surfaces when used. Examples include spray products with certain fluorosilane compounds, in which it has been shown, that they could have effects that are harmful to health.

Textiles: In addition to the existence of pigments in textile inks, nano silver is used as an antibacterial agent in textiles. This application is discussed in the example box in Chapter 2.

Paints / varnishes, printing inks and inks: Since most pigments fall within the nano definition, most paint / varnish-products and printing inks contain nanomaterials [15]. A portion of the fillers used in the products would probably also fall within the definition. In some types of product, pigments are present as nano-sized particles where their nano properties are exploited intentionally. These include UV protective paints and wood preservation products, inks for inkjet printers and textile printing and metallic effect paints. In some types of paint, photocatalytic titanium dioxide is used to form "self-cleaning" surfaces.

Food: A range of food additives contain nano particles [7, 16, 21]. These include titanium dioxide (E171), silicon compounds and silicates (E551 used as an anti-caking agent, anti-foaming agent, aroma carrier and thickener) and calcium carbonate (stabiliser, anti-caking agent).

Food contact materials: There is no evidence of the use of nanomaterials in food wrapping products in Denmark. There are however, pigments and possibly other nanomaterials in adhesives, polymers and paper used for labels, labelling and packaging, but they are not specified further [7].

Antibacterial agents: Nano silver is used as mentioned in Chapter 2 in textiles, but it can also be present as antibacterial agent in many other products such as kitchen equipment, refrigerators, deep freezers and coffee makers, hygienic surfaces and toothbrushes in which the silver is bound to the surface and silver ions are released slowly. A study of a variety of types of consumer product however, found no concrete examples of products of this type with nano silver on the Danish market [7]. Nano silver may also be present in cleaning products [7].

Pigments: Pigments may be used for a wide variety of purposes. This is especially true in paints, plastics and rubber, coloured paper and cardboard and building materials [13]. Pigments in the finished products may be bound in a matrix from which they are not directly released as unbound particles.

Carbon nanotubes (CNT): Carbon nanotubes are used mainly to strengthen composite materials, but also to exploit their electrical and optical properties. In consumer products the best known applications are in sporting equipment [11, 16, 30], but they can also be used for example, in electronics and paint.

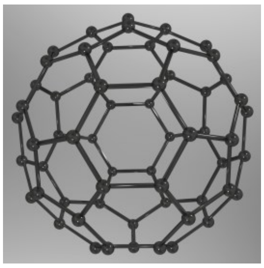
Other applications of nanomaterials

The "Better control of nanomaterials" initiative has focused primarily on consumer products. To a limited extent however, it also looked at other examples of applications that could result in releases to the environment.

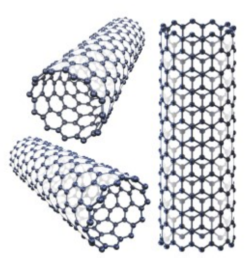
Water treatment: In Danmark, photocatalytic UV lamps containing titanium dioxide nanoparticles have been used successfully as catalysts in some public swimming pools. In addition, large-scale systems to treat ballast water have been on the market for several years [7].

Medical devices: Currently many different medical devices containing nanomaterials are in use. Nanomaterials that are found in products on the Danish market include silicates and zirconium dioxide (mechanical properties of seals, adhesives and implants), silver (antibacterial effect), copper (filters in colostomy bags), calci-

The more advanced nanomaterials, which are not only fine grained particles of known materials, are used to a limited extent in consumer products. Three of these advanced nano products are mentioned below.



Spherical **fullerenes** are primarily used in biomedical research and are probably not present in consumer products.



Carbon nanotubes are used in sporting equipment among other products, but they are embedded in the composite plastic and not released in significant quantities during normal use.

Quantum dots are nano scale semiconductor materials which are principally used in LED bulbs, where they are completely embedded in the material and are not released during use.

um alginate (carriers and moisture absorbents) and also zinc oxide, titanium dioxide and iron oxide (pigments) [7].

Nano product register

There is limited knowledge about the extent of use of nanomaterials in consumer products on the Danish market. Part of the "Better control of nanomaterials" initiative was therefore, the setting up of a nano product register. The purpose of the register is to quantify the amounts, types and applications of certain types of consumer product on the Danish market which contain and release nanomaterials. It is intended that in the long term the information in the register will form the basis for further assessment of whether the content of nanomaterials in products pose a risk to consumers and to the environment. Experience with the nano product register is described in more detail in Chapter 6.

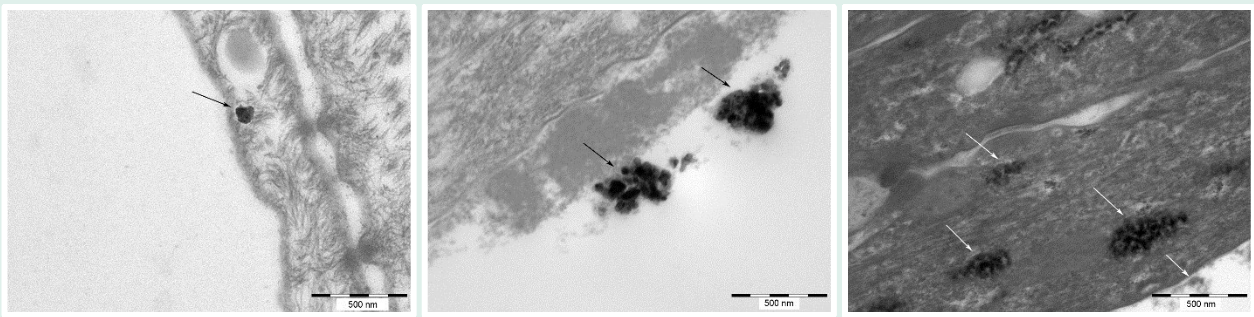
Example: Various forms and uses of titanium dioxide

Titanium dioxide is one of the most commonly used and best described nanomaterials, and it is found in many different types of consumer product. The use of nano titanium dioxide is described in a number of studies under the "Better control of nanomaterials" initiative. The uses of the photocatalytic form (anatase) in consumer products has been the focal point of one of the studies [13]. Another study has examined skin absorption of nano titanium dioxide from sunscreen products [20]. Titanium dioxide occurs primarily in two crystal forms: rutile and anatase that are different both in terms of technical properties and the effects of the substances on the environment and on human health.

Pigment: The most important use of titanium dioxide in terms of quantity, which constitute about 99% of consumption, is as pigment in paints, coatings, plastics and printing inks [15]. Due to the size of the primary particles, titanium dioxide, in common with other pigments, falls within the definition of nano. In practice however, titanium dioxide occurs as larger aggregated particles that appear white.

Photocatalytic effect: The anatase form of nano titanium dioxide exhibits a photocatalytic effect, which upon illumination, and contact with moisture forms free radicals, which have an inhibitory effect on microorganisms. The substance is used as a biocide. The applications of the photocatalytic effect include paints, coatings, air cleaners, construction materials and water purification systems.

UV protection: Nano-titanium dioxide is used for UV protection in sunscreen products, paints and other products. As the particles are much smaller than the wavelength of visible light, they do not reflect visible light (and thus do not appear white) but still function as a filter for UV light. The anatase form is primarily used for this purpose. In order to avoid the photocatalytic effect on the skin, the nano titanium dioxide used in cosmetics is surface treated. A number of other nanomaterials such as nano cerium dioxide have similar properties. Nano cerium dioxide is in Denmark used as UV protectant in paint [11].



Transmission electron microscopy (TEM) of skin model showing titanium dioxide particles marked with arrows [20]

Disposal of products by the end of their service life

A study summarised the existing knowledge on the presence of nanomaterials in waste [9]. The study concludes that there is very limited information available on what happens to nanomaterials in the waste treatment system. It is judged that the most frequently occurring nanomaterials in waste, (except for pigments and other materials without intentional nano effects), were as follows:

- nano silver (metal, textiles, electronics waste),
- nano titanium dioxide (building and demolition waste, plastics, textiles, electronics waste and scrapped motor vehicles),
- nano clay (building and demolition waste, plastics and tyres),
- nano zirconium oxide (building and demolition waste and electronics waste), and
- nano cerium dioxide (building and demolition waste).

In addition, carbon nanotubes could occur to some extent. During the waste incineration process, there is consensus among researchers that the inorganic nanomaterials, titanium dioxide, zinc oxide and silver, primarily end up in the slag and to some extent in the flue gas cleaning products, the latter is often exported from Denmark. Only very small amounts are released via flue gas from incineration plants. Carbon nanotubes are expected to be destroyed in the process if the temperature is constant and sufficiently high. Those that are not destroyed end up in the slag. Since the vast majority of slag in Denmark is recycled after sorting and crushing, there is potential risk of impact in the workplace environment during recycling. In addition, environmental impacts is possible from the leaching of nanomaterials from the slag, when recycled for road construction.

4. Risk to consumers

One of the main objectives with "Better control of nanomaterials" was to evaluate possible risks to the Danish consumers in relation to use of products containing nanomaterials.

Chapter 3 described the knowledge established by a number of surveys with regard to the occurrence of nanomaterials in consumer products. A number of projects have further aimed to illustrate what nanomaterials the Danish consumers are exposed to and whether this causes a risk. Therefore, a number of projects have focused on the use of specific nanomaterials or product types: carbon nanotubes [30], nano silver in textiles [3, 24], the anatase-form of nano titanium dioxide [13] and aerosol products [19]. Furthermore, a larger general study of consumer products with nanomaterials was carried out [16, 17, 21]. This chapter is primarily based on the results from the latter general project, which includes cases that are illustrated in more detail in the specific projects.

Furthermore, the "Better control of nanomaterials"-initiative has provided an overview of the knowledge about releases of nanomaterials from mixtures and articles [25], and to what extend the nanomaterials are absorbed as a result of oral intake [4] or as a result of dermal exposure [5, 20].

The "Better control of nanomaterials"-initiative has not initiated specific projects in order to assess uptake and effects caused by inhalation of nanomaterials, which typically is regarded the most substantial health-related exposure route. The reason is that inhalation of nano particles is investigated as a part of the activities at the Danish NanoSafety Centre in a 30 million DKK programme which has been executed simultaneously with the "Better control of nanomaterials" initiative. The Danish NanoSafety Centre focuses on the working environment, however the results can also be used to illustrate the possible exposure of consumers by inhalation.

The two initiatives have been coordinated and knowledge about effects and risks caused by inhalation have been included in assessments of risks for consumers as further described in this chapter. Furthermore, by the end of the chapter the consumer exposure of nanomaterials will be put into perspective in relation to exposure to nanomaterials in the working environment.

Nanomaterials in consumer products – accuracy of knowledge

As it appears in chapter 3, much knowledge exists about where nanomaterials are used or could be used. However, the underlying reports show that it is often very difficult to determine with certainty whether the individual nanomaterials actually are used in the consumer products. This is caused by a number of reasons:

Inventories and databases: A substantial source for knowledge about possible content of nanomaterials in products is surveys, inventories and databases, which to a large extent are based on the companies' nano claims on their webpages [16, 21]. Products, where the producer or supplier do not claim nano, are therefore not included in these inventories /databases. On the other hand, it is not known for sure whether the products claimed *nano* actually contain nanomaterials, as these inventories /databases do not attempt to verify if the products are containing nanomaterials. Other uncertainties by using this type of data are that the type of nanomaterial the product contains is seldom indicated and furthermore, the quantities and concentrations of nanomaterials in the products are often uncertain.

Knowledge among producers, importers and within the supply chain: Information about content of nanomaterials in raw materials and products is only exchanged to a limited extent in the supply chains which are often international and diversified. The executed surveys that have contacted companies presumed to sell products with nanomaterials, have therefore had their difficulties in identifying specific products on the market in which it with certainty is known that they contain a given nanomaterial [11, 13, 15]. The same picture emerged in interviews undertaken as part of the just finished project on the companies' administrative burdens associated with the nano product register [29].

In a general project concerning consumer risks (across nanomaterials and applications) [16, 21], the above information sources were supplemented with search in the literature. In general, a significant part of the information on the product's content of nanomaterials is not specifically based on information about products sold in Denmark.

The uncertainties about the occurrence of nanomaterials in consumer products naturally makes the starting point for assessment of consumer risks uncertain. The general project for assessment of consumer risks [16, 21] was performed under the assumption that Danish consumer products do not deviate significantly from consumer products sold in other countries and consequently, information from foreign sources and the international literature can be used in case there is no specific information on Danish consumer products.

Focus has been on products where it was positively known that they contain nanomaterials and where the chemistry of the contained nanomaterial was known. Potentially, nanomaterials are used in many different consumer products and 21 products were therefore selected for detailed assessment within the boundaries of the project. The selection was made in dialogue with The Danish Environmental Protection Agency and an international advisory group. The 21 products represent different types of nanomaterials and applications with high and low exposures, respectively, as well as different exposure routes. The selected products are shown in the table later in this chapter. It must be emphasized that these products do not fully represent all possible consumer exposures.

Exposure of consumers

Consumers can be exposed to nanomaterials by:

- **Oral intake**: Intake via the mouth either intentionally, e.g. nanomaterials in food additives, or unintentionally, e.g. when sunscreen is used on the lips.
- **Dermal exposure**: Intentionally, e.g. nanomaterials in sunscreen and other cosmetics, or unintentionally, e.g. when handling paint.
- **Inhalation**: Typically unintentionally in connection with use of dusty products (e.g. cement) or in situations, where energy is used, e.g. by using nanomaterials in sprays or by sanding surfaces painted with paint containing nanomaterials.
- **Eye exposure:** Typical unintentionally via dusty products, via stains or use of cosmetics close to the eye.

There are considerable uncertainties associated with calculation of exposure. The uncertainties concern i) the percentage content of nanomaterials in the products, ii) knowledge about the level of releases from products where the nanomaterial can occur e.g. in a fixed matrix, iii) the level or the concentration the consumer actually is exposed to (few data in the literature),

Application of nano-titanium dioxide in sunscreen is one of the most well investigated applications of nanomaterials.

As nano titanium dioxide is not absorbed through the skin [20], the risk by dermal absorption is assessed to be insignificant.

On the other hand, a general health assessment of nanomaterials [21] reached the conclusion that intake of titanium dioxide in sunscreen through the mouth may pose a possible risk.

and finally iv) whether the consumer is exposed to the free nanomaterial or to the nanomaterial bound in a matrix (e.g. sanding dust), where a part of the nanomaterial may be bound in the paint matrix.

In order to consider these uncertainties, conservative worst-case assumptions were used when assessing exposure levels in the general project [16, 21]. More information on releases from product are found in the investigation of releases of nanomaterials from products [25].

Effects of nanomaterials

The general project on consumer risks has reviewed knowledge about effects of seven prevalent nanomaterials in 21 products [17], and as mentioned initially, a number of projects have specifically investigated absorption as a result of oral intake [4] or dermal exposure [5, 20].

Especially in relation to dermal exposure, which is a very frequent exposure route for consumers, it is important to note that the knowledge available today indicates that nanomaterials are not, or only to a very little extent, absorbed in nanoform through the skin. Experiments with soluble nanomaterials as nano silver and nano zinc oxide have shown that skin exposure can lead to absorption of silver and zinc. However, as far as can be determined, it is not yet proven that the substances are absorbed in nanoform, rather as metal ions. Furthermore, the present knowledge indicates that nanomaterials do not cause substantial irritation or damage to the skin.

It is not possible to make general statements about how hazardous oral intake of nanomaterials is, as the hazard is very substance and material specific. For most nanomaterials, oral intake is not seen as the most important exposure route. However, as described below and shown in the below table, it cannot be ruled out that there is a risk connected with large intentional or unintentional oral intake.

Inhalation is generally seen as the exposure route that provides the most significant health effects. Besides the chemical contents of the nanomaterial, the very small size and the shape of the nanomaterial play a substantial role. As the most serious example, there are indications that certain types of fibre-like carbon nanotubes may have the same mode of action as asbestos and thus lead to lung cancer [17, 30]. However, the very size of nanomaterials make them capable of penetrating deep down the respiratory tract where they, just as ultra-fine particles from the traffic, can lead to irritation / inflammation and other airway disorders that in the long term in some cases can lead to cancer and cardiovascular diseases.

There is a number of challenges associated with extrapolating from laboratory tests, which analyse the hazard of specific nanomaterials, to the materials actually present in consumer products and the materials the consumers are exposed to. Compared to the traditional chemicals, a number of additional uncertainties are associated with the assessments. Furthermore, there is uncertainty about which nanomaterials are specifically present in the products compared to those applied in the laboratory tests. In addition, the laboratory tests are often carried out on dispersed particles while the nanomaterials in the consumer products are often present in agglomerated or aggregated form (see Chapter 3) or embedded in a matrix. Moreover, there are uncertainties related to which metrics are used to express the no-effect level as the hazard of nanomaterials can be represented not only by a mass concentration, as for instance the number of particles and the total surface area of the particles may be of significance as well [17, 21].

The general project on consumer risk has in general used worst case considerations when assessing the level of the nanomaterials' possible effects [17, 21].

Risk to consumers

The risk assessments have, as far as possible, followed the current guidelines for risk assessment of chemicals in a regulatory context, e.g. the principles normally applied under REACH [21].

As mentioned above, there are special uncertainties associated with risk assessments of nanomaterials and very conservative / worst-case assumptions are therefore applied. The following considerations do, therefore, not apply to all products within a given product type, but typically to products with a large content of nanomaterials and under special application patterns. However, it is assessed that there can still be uncertainties not taken into account, *why the results from the risk assessment must be considered as indications rather than hard facts.* This is also indicated by the wording used in the table overleaf presenting the results of the risk assessment.

Products assessed in the general consumer product project

Product/scenario	Exposure route			
	Oral	Dermal	Inhalation	Eye
Chewing gum (nano-TiO_2 in E171)	Risk uncertain	Not relevant	Not relevant	Not relevant
Food additive (nano-silica in E551)	Risk uncertain	Not relevant	Not relevant	Not relevant
Food supplement (nano-Ag)*	Risk unlikely	Not relevant	Not relevant	Not relevant
Food contact material (nano-silica)	Risk unlikely	Not relevant	Not relevant	Not relevant
Sunscreen lotion (nano-TiO_2)	Risk possible	Risk unlikely	Not relevant	Not relevant
Sunscreen pump spray (nano-ZnO)	Risk possible	Risk unlikely	Risk uncertain	Not relevant
Mascara (carbon black)	Not relevant	Risk unlikely	Not relevant	Risk unlikely
Sunscreen lipstick (nano-TiO_2)	Risk possible	Risk unlikely	Not relevant	Not relevant
Face powder (nano-silica)	Risk unlikely	Risk unlikely	Risk possible	Risk unlikely
Paint, rolling (nano-TiO_2)	Not relevant	Risk unlikely	Not relevant	Risk unlikely
Sanding surface treated with water based primer (nano-TiO_2)	Risk unlikely	Risk unlikely	Risk likely	Not relevant
Paint, spray gun (nano-Ag)	Risk unlikely	Risk unlikely	Risk likely	Risk unlikely
Impregnation, pump spray (nano-silica)	Risk unlikely	Risk unlikely	Risk possible	Risk unlikely
Air-cleaner/nano-filtering (nano-Ag)	Not relevant	Not relevant	Risk unlikely	Not relevant
Disinfectant pump spray (nano-Ag)	Risk unlikely	Risk unlikely	Risk uncertain	Not relevant
Disinfectant propellant spray (nano-Ag)	Risk unlikely	Risk unlikely	Risk possible	Not relevant
Textile (nano-Ag)	Risk unlikely	Risk unlikely	Risk unlikely	Not relevant
Cement (nano-TiO_2)	Not relevant	Risk unlikely	Risk possible	Risk unlikely
Wound dressing (nano-Ag)	Not relevant	Risk unlikely	Not relevant	Not relevant
Dental fillings (nano-silica and nano-ZrO_2)	Risk unlikely	Risk unlikely	Risk uncertain	Not relevant
Golf club fitting (carbon nanotubes)	Risk unlikely	Risk unlikely	Risk uncertain	Not relevant

Risk unlikely | Risk uncertain | Risk possible | Risk likely | Not relevant

* Not allowed, but available via the internet.

The table shows that even under worst-case assumptions, the risk for a number of product types is considered unlikely.

Furthermore, the table shows that risks due to dermal exposure apparently are not significant, which is in accordance with the existing knowledge indicating that nanomaterials are not absorbed through the skin and do not, to a substantial degree, lead to damages of the skin. Substantial risk in connection to eye exposure does not seem to be an issue, it must however be noticed that very limited knowledge is available about possible damages as a result of eye exposure.

More surprisingly, the assessments indicate that there is an uncertainty as to the risk of nanomaterials in food additives (nano silica and nano titanium oxide). It must be emphasized that the risk assessments carried out have been very conservative and the uncertainties are essentially due to new data that were not available when the food additives were assessed in a regulatory context. Within the limits of the consumer project, is was not possible to assess the relevance of these data, however reassessment of these food additives is currently done at EU level.

In addition, it is surprising that use of sunscreen (with nano titanium oxide and nano zinc oxide) with possible oral intake (licking on fingers and sunscreen on lips) is assessed to pose a possible risk. Again it must be emphasized that the assessments done in the general project are very conservative. It can be mentioned that the EU Scientific Committee on Consumer Safety has assessed the application of nano titanium oxide in sunscreen. The committee considered it most relevant to assess dermal exposure and thus not relevant to assess possible oral intake further. In the consumer project report [21], it is acknowledged that sunscreen has a positive effect by protecting against skin cancer and therefore the report recommends to use the products in a way that lower the unintended oral intake.

Less surprisingly, the project reaches the conclusion that there can be a risk associated with inhalation of nanomaterials by applications where nanomaterials are released. It is assessed that there likely is a risk when paint is applied with a spray gun without using respiratory protective equipment. It must be mentioned that this application is assessed to pose a risk even for paints without nanomaterials. Furthermore, it is assessed that there most likely will be a risk if a surface treated with a water-based primer where the nanomaterials are not fixed in a matrix at the painted surface is sanded without using respiratory personal protection equipment. This conclusion is, however, not applicable in general to sanding surfaces treated with products containing nanomaterials. For a number of other products it is assessed that there is a "possible risk" or the risk is considered uncertain. This applies to uses of a number of spray products, face powder and handling of cement as well as polishing of tooth fillings and mechanical processing of a golf club. Again, it must be emphasized that the assessments carried out are very conservative and in general very limited information about exposure levels and risks is available. More information about consumer products that leads to inhalation of nanomaterials is therefore desirable. Finally, it should be noted that the use of spray products in general can lead to risks and that the project on assessments of aerosol-products was not able to indicate whether an extra risk was connected to spray products with content of nanomaterials [19].

Eventually, it should be mentioned that nanomaterials are often used in solid goods/articles, where the nanomaterial is a part of a solid matrix, e.g. in plastic products. Unless these products are subject to mechanical processing, the nanomaterial will typically only slowly be released from the product and therefore normally not lead to any consumer risk. However, this does not rule out the possibility of risks connected to production or disposal of these products [21].

Perspective in relation to other sources

One of the projects under the "Better control of nanomaterials" initiative has investigated the levels of unintentionally formed nano particles to which the general population is exposed [18]. The results of that project are discussed in relation to the estimated consumer exposures and risks described above [21].

The general population can be exposed to quite high levels of ultra-fine particles outdoors (e.g. from traffic), in the indoor environment (e.g. when using candles), by cooking or when using electrical instruments or heating systems. The available knowledge suggests that especially indoor exposures, measured by the particle number, can reach very high levels. Based on the available data, the exposures seem to reach a considerable higher level and for a longer duration than the exposure that may occur using consumer products with nanomaterials. However, this does not apply to all situations [21].

It is concluded that even though comparison of levels of exposure for unintendedly formed nanoparticles and nanoparticles from consumer products, respectively, may provide an idea about the significance of different sources, it is necessary to be careful comparing these exposures without considering that the particles originate from different sources. Because the particles come from different sources, the particles are different from each other regarding the chemical composition, particle size, etc. and thereby they differ with regard to how hazardous they are for humans. In this connection, it must be mentioned that the knowledge about ultrafine particles in the indoor environment is very limited.

Perspective in relation to exposure and risks in the working environment

The most serious health damaging effects are seen by inhalation of nanomaterials and espe-

Application of aerosols cans with nano particles are assessed most likely to result in a risk for the consumers through inhalation.

A number of aerosols cans promoted as "nano" do not contain nano particles, however, when using the aerosols, nano structures are formed at the surface of the painted subject. These products may be health damaging.

Spray paint also without the use of aerosols are assessed to cause risk dependent on the protection equipment used.

cially by inhalation of the pure nanomaterials. Consequently, it is in the working environment during production of products containing nanomaterials, and maybe also by waste management, the highest risk of inhalation of nanomaterials exists. Often, the exposure is larger in the working environment compared to the exposure that consumers experience and workers may be exposed through a 40-year long work life. Added up, it means that exposure to nanomaterials through inhalation is potentially higher in the working environment than in consumer settings. On the other hand, nanomaterials are typically used with other protective measures (ventilation, personal protection equipment, etc.) in the working environment than those used by the consumers [21]. As mentioned in the introduction, the Danish NanoSafety Centre (http://nanosikkerhed.nu/) at the National Research Centre for the Working Environment addresses occupational health aspects of safe management of nanomaterials, why "Better control of nanomaterials" has focused on consumers and the environment.

5. Risk to the environment

Risks connected to nanomaterials in the environment are investigated through a number of studies in the project "Nanomaterial – occurrence and effect in the Danish environment" (abbreviated NanoDEN).

Fundamentally, an environmental risk assessment of a substance is carried out by comparing the estimated or measured concentration of the substance in the environment (PEC-value) with the highest concentration anticipated not to affect the organisms in the environment (PNEC value). If the potential concentrations in the environment are higher than the concentrations that may cause considerable effect, there is an environmental risk.

For the environmental risk assessment in the project, 10 industrially produced nanomaterials were selected. The materials are listed in the box overleaf. These 10 nanomaterials represent partly nanomaterials used in high tonnages, partly materials with a wide spectre of possible applications in relevant consumer products, industrial processes and environmental technology applications. Finally, they are selected because they represent a wide range of physical-chemical and environmental characteristics. The selected nanomaterials are therefore considered as representative as regards assessing the extent to which nanomaterials pose an environmental risk in Denmark.

Discharge of nanomaterials and concentrations in the environment

As it is not possible to measure nanomaterials in discharges and in the environment with the current techniques, it has been necessary to calculate the potential concentrations of nanomaterials in the environment in Denmark and in the surrounding coastal waters based on both general knowledge and specific knowledge on the use of the materials in Denmark

For each application of the substances, the quantities potentially used in Denmark are estimated and it is assessed how much of the used quantities will be discharged to the environment by the various release pathways [10, 11, 12]. Some of the substances, e.g. copper carbonate are not used in nano size in Denmark for the stated purpose (wood preservation) today, however in the calculations it is assumed that materials in nano size in the future could replace the present use of substances.

Key parameters of an environmental risk assessment

PEC - Predicted Environmental Concentration – the concentration expected in the environment based on measurements or model calculations

PNEC - Predicted No-Effect Concentration – is the highest concentration expected not to cause considerable effects on organisms in the environment

RQ - Risk Quotient – is calculated as PEC/PNEC. If RQ is higher than 1, it is assessed that there is a risk for organisms in the environment

In order to provide a better basis for calculating the quantities of nanomaterials that organisms in the environment can be exposed to, a description and assessment of the substances' behaviour and fate in the environment [8] was prepared.

All values in the model calculations are represented with probability distributions (95 % confidence interval and most likely value). The quantities potentially released and the resulting concentrations in the environment were subsequently calculated with a computer program. The concentrations in the environment are also represented as probability distributions. With the employed model, it is taken into account that it is unlikely for all parameters to reach their maximum values at the same time and hereby it is possible to calculate realistic worst-case scenarios.

None of the selected nanomaterials are produced in Denmark. As a general trend (with few exceptions), companies in the chemical sector have moved substantial parts of their production to Eastern Europe or Asia, and the activities in Denmark are primarily limited to research and formulation of chemical products in ready-made products. The study only identified one company with direct discharge to the water environment of the nanomaterials comprised by this report and there is most likely only few companies using the materials involved that discharge treated wastewater directly in to surface water. Overall, it is assessed that discharges from production processes in Denmark are small compared to discharges from the later use of the chemical mixtures and articles, including diffuse discharges.

The critical applications of nanomaterials are basically those that lead to direct discharge to one or more parts of the environment i.e. without first passing through a sewage treatment plant, waste incineration plant or other forms of technical emission controls. Examples of such critical applications are outdoor paints or other outdoor surface coatings, impregnation of wood for outdoor use, antifouling paints for ships, catalysts and fuel additives for cars, car tyres and artificial turf. Some of these applications cause exposure of the freshwater environment due to discharge of untreated run-off from roofs and roads (e.g. cerium dioxide and carbon black), while other cause exposure of the soil environment (copper carbonate) or the marine environment (ship paint).

Assessed nanomaterials

Photo stable titanium dioxide (TiO_2): Used as UV-filter e.g. in sunscreen
Photo-catalytic titanium dioxide (TiO_2): Used as biocide e.g. in self-cleaning painted surfaces
Zinc oxide (ZnO): Used as UV-filter e.g. in sunscreen
Silver (Ag): Used as biocide e.g. in textiles and on hygienic surfaces
Carbon nanotubes (CNT, carbon nanotubes): Primarily used as a component in batteries and as a reinforcement of composites e.g. in sports equipment
Copper carbonate ($CuCO_3$): Can be used as biocide in wood preservatives*
Zero-valent iron (nZVI, nano zero valent iron): Used for soil and groundwater remediation
Cerium dioxide (CeO_2): Used as UV-filter e.g. in wood preservatives
Quantum dots (QD, quantum dots): Used in LED-bulbs and other electronics
Carbon black (CB): Broad use as black pigment and vulcanization agent in tyres and other rubber products
** Due to lack of data about effects of nano copper carbonate it was necessary to use effect data for nano copper oxide for the risk assessment of this material.*

Effects of nanomaterials

Based on a literature review, it was assessed that in principle it is possible to use the same methods for nanomaterials as the methods accepted in current EU-regulation for estimating the concentration at which a chemical substance does not result in effects (PNEC) [22]. However, the methods do not consider nano-specific processes such as agglomeration of the particles that leads to a reduced risk because it results in fewer and larger particles. The results of the laboratory tests are therefore not always representative for natural conditions. The methods for determining PNEC values in the project are not yet documented for nanomaterials and the calculated values must therefore be considered as guiding for the order of magnitude of the values. The methods must be developed further at EU-level before definitive values can be calculated and used to establish the concentration in the environment that is considered not problematic.

With regard to the establishment of PNEC-values for nanomaterials, it is a significant problem that most effect studies are based on test guidelines prepared for soluble chemicals, which are not always reliable when it comes to nanomaterials [22]. Furthermore, the number of studies is very limited and does not cover all test organisms, environmental matrices and effects. Therefore, there is only robust data from freshwater environments that cannot be extrapolated directly into other environments. Therefore, it has not been possible to quantify the risk through risk quotients (RQ) for organisms in the marine environment, soil environment, sediments and sewage treatment plants.

By using the available data, silver nano particles were assessed as the most hazardous among the investigated nanomaterials in the freshwater environment, followed by carbon nanotubes and copper oxide. Titanium dioxide was assessed to be the least ecotoxic of the materials. Due to lack of data, it was not possible to establish PNEC-values for carbon black and quantum dots. In order to account for the uncertainties associated with extrapolating from lab test results to natural conditions, a safety factor of 100 for silver, copper oxide and zero-valent iron was used while for the rest of the substances a safety factor of 50 was applied.

Potential risks to the environment

Based on the current knowledge about effects and with the current applications and quantities consumed, it was assessed that none of the investigated nanomaterials pose an environmental risk in the freshwater environment in Denmark (i.e. they are not both very hazardous for aquatic organisms and have high occurrence in the environment) [23]. Potentially critical nanomaterials are found among the materials that either are very hazardous (silver, copper oxide and carbon nanotubes), or materials that are less hazardous but where the uses result in a considerable exposure of organisms in the environment (titanium dioxide and carbon black). For both groups the consumption of the substances has to increase considerably compared to the current level in order to actually pose a risk to the freshwater environment. It is assessed unlikely for the rest of the selected nanomaterials that they should pose a general risk for organisms in the freshwater environment. However, the general assessment does not take into account local impacts under special conditions and it has not been possible to assess the risk of toxic effects in soil and sediment-dwelling organisms or of bioaccumulation due to the above-mentioned lack of relevant effect data.

Using the most likely value for the environmental concentration (PEC), only 1-2 materials (copper and maybe carbon black), have risk quotients (RQ) larger than 1 in the undiluted effluent from sewage treatment plants (i.e. a potential environmental risk in this point exists). Using the maximal concentration, there will also be a risk for silver and titanium dioxide, however the maximum risk quotient (for copper) is still only approximately 12. A risk reduction of this magnitude will normally be possible to obtain with discharges from sewage treatment plants due to dilution of the effluent in the receiving water.

None of the calculated average concentrations in surface water will therefore lead to risk quotients anywhere near the value of 1 [23], when the mixing of the effluent and surface water has taken place.

Data gaps

In general, data concerning applications, discharges and effects of nanomaterials are lacking, however of greatest importance for the total assessment is the lack of data about effects in sediments, the marine environment and the soil environment because the risk quotients determined for the freshwater environment cannot be extrapolated to other parts of the environment with the known methods of today. Therefore, a uncertainty still exists as to which extent some of the nanomaterials may cause a risk in other parts of the environment. However, it must be noted that in the risk assessment it is conservatively assumed that the nanomaterials remain on nanoform and not aggregated to form larger particles.

6. Legislation and perspective

The purpose with this chapter is to provide an overview of activities with regard to legislation, research and standardisation in the nano-field to draw a perspective of the "Better control of nanomaterials"-initiative.

Current and future legislation

As mentioned initially, the European Commission has clarified that legislation on chemical substances also applies to nanomaterials as *nano* in nanomaterials only refers to another *form/size* (the nanoform) of a given chemical [32, 33, 34]. At the same time, it is acknowledged that these legislations not always address *specific properties of nanomaterials* sufficiently, and in some cases there has been a request to label certain products for content of nanomaterials.

REACH: In relation to the chemical legislation in EU (REACH, Regulation no. 1907/2006), discussions are in progress about adjustment of the information requirements for chemical substances in nanoform as well as possible requirements about specific assessment of the nanoform based on the generated data. Suggestions for changes of the information requirements have been in public consultation and the consequences for industry and society have been assessed in a number of EU impact assessments. Based on these activities, a concrete initiative with suggestion for changes of the information requirements under REACH from the European Commission is awaited. Acknowledging that nanomaterials can have unique properties, the European Chemicals Agency (ECHA) already recognizes this to some extent in their guidelines and assessments. Under the "Better control of nanomaterials" initiative, a suggestion for relevant information requirements for nanomaterials in a regulatory context was prepared [6].

Cosmetics: The Cosmetics Regulation (Regulation no. 1223/2009) stipulates that the content of nanomaterials in cosmetic products is notified to the European Commission and that the content is declared in the list of ingredients by the chemical name followed by nano in brackets e.g. "titanium dioxide (nano)".

Biocides: The Biocidal Products Regulation (Regulation no. 528/2012) stipulates labelling of chemical active substances in nanoform. Furthermore, the regulation requires that the nanoform is assessed and approved specifically. Nano silver, for example, must therefore be addressed specifically and does not fall under the assessment and approval of silver as such.

Food: The Food Additive Regulation (Regulation no. 1333/2008) and the regulation on plastic materials and articles intended to come into contact with food (Regulation no. 10/2011) stipulates in the same way specific assessment and approval of the nanoform of approved substances. The regulation on the provision of food information to consumers (Regulation no. 1169/2011) stipulates that nanomaterials shall be clearly indicated in the list of ingredients. Furthermore, the "Novel Food"-legislation is under revision, this also comprises considerations in relation to specific requirements regarding nanomaterials.

Medical equipment: The regulation regarding medical equipment is also undergoing a revision with serious consideration about introducing requirements for labelling and specific assessment of equipment that contains nanomaterials.

Electronics: The legislation on restriction of certain hazardous substances in electrical and electronic equipment (ROHS Directive 65/2011) and the directive on disposal of electronic waste (WEEE Directive 19/2012) mention nanomaterials, but have not yet introduced specific requirements.

EU working groups

In order to support the above-mentioned legislative activities, a number of working groups are established at EU-level. Some of these working groups and their activities are briefly described in the following.

A number of working groups are established in relation to each of the above mentioned instruments with the aim of discussing the implementation of the requirements and possible needs for adjustments. Nanomaterials have been discussed in most of those working groups and as indicated above, it also led to regulatory changes.

Besides these working groups, in relation to REACH a special sub-group is appointed, CASG-nano (Competent Authority Sub-Group for Nanomaterials) to address nanomaterials. The working group is led by the European Commission and consists of employees from the Member States' competent authorities in the field of chemicals. The European Chemicals Agency, which has the administrative responsibility for the REACH Regulation, has established a working group (ECHA Nanomaterials Working Group), in which experts discuss the management of nanomaterials under REACH.

The EU Scientific Committee on Consumer Safety supports the Commission with scientific opinions about certain components in cosmetics including nanomaterials. As an example, opinions about nano titanium dioxide and nano zinc oxide as UV-filters in cosmetics are available. The committee has also been requested to assess various forms of nano silica, among others because the received notifications showed a prevalent use of certain types of nano silica in cosmetics [37].

Nano registers: EU and nationally

There is a widespread political will to be transparent about in which products nanomaterials are actually present. For quite some time, it has been discussed whether a register should be established at EU-level. Based on the Second Regulatory Review on Nanomaterials [34], the European Commission has carried out an impact assessment and a public consultation as well as executed a number of stakeholder workshops to create a basis for deciding on a possible establishment of a nano register at EU-level [38]. At the moment, the further perspective for establishing such a register at EU-level is not clear.

In the meantime, both France and Belgium have like Denmark established national registers, and the same is considered in a number of other EU countries, including Italy, Germany and Sweden.

One of the purposes of the "Better control of nanomaterials"-initiative has been "... development of a nano product database in cooperation with other countries". The Danish Environmental Protection Agency has informed that as part of the drafting of the Danish Statutory Order on the nano product register, a number of meetings with France, Belgium and Italy were conducted and further exchange of experience with France took place. Furthermore, the Danish Environmental Protection Agency has held a meeting with the European Chemicals Agency. Based on this, it was decided that the Danish register should focus on nano products for consumers, whereas the French register is considerably more comprehensive as it follows the nanomaterial in its applications and also comprises professional applications. On the other hand, the French register does not comprise articles - i.e. goods in solid form – which are comprised by the Danish register. The information requirements for nanomaterials in products to be notified to the Danish register are, however, to the extent possible harmonised with the data requirements of national registers in other countries. This is

REACH and other legislation about chemical substances also apply to nanomaterials but do not address the specific properties of the substances when in nanoform.

An EU process is in progress in order to adjust the requirements for information and assessment of nanomaterials in the general chemical legislation REACH.

done, in order to ensure a certain degree of consistency of data if there at some point should be established a common EU register.

In addition, it should be mentioned that the drafting and implementation of the Statutory Order was done in dialogue with the industry and other stakeholders. A process that companies and trade organization have expressed their satisfaction with [29]. As a part of the basis for the decision, some assessments of possible consequences for Danish companies, among others various possible exemptions from reporting, were prepared [1,2]. This process lead among others to a number of modifications to the draft of the Statutory Order so it e.g. only is necessary to report products that release nanomaterials during use. Furthermore, a number of specific product types are exempted. In particular, it concerns a number of product types in which pigments are used widely. As mentioned earlier, the Danish Environment Protection Agency initiated a specific project for mapping pigments in nano size [15]. The Statutory Order also exempts products already (or expected to be) covered by legislation specifically addressing nanomaterials, including food, cosmetics and biocides (see above). A supplementary study was initiated in order to survey the current applications within these areas [7].

Experiences with the Danish nano product register

The first deadline for reporting to the Danish nano product register was by the end of August 2015. The Danish Environment Protection Agency informs that 117 registrations from 8 companies have been submitted. Two main groups of products within construction goods (106 reports) and consumer goods (11 reports), respectively, are registered. As a consequence of the low number of reporting companies, and due to confidentiality issues, limited information can be provided regarding the registrations. Some of the reasons for the low number of reports are described in the report that assesses the administrative burdens of reporting to the nano product register [29]. Among others, that project was based on interviews with 11 trade organizations, five of the reporting companies and a number of companies that assessed whether they had to register and concluded that they did not need to.

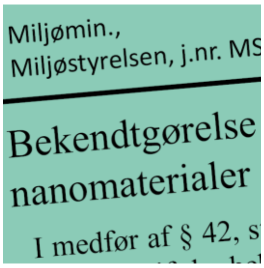
The interviewed companies were typically front runners with special expertise and/or interest in meeting environmental requirements. Their and the trade organizations' assessment is that many companies are not aware of this legislation and/or do not have enough knowledge about "nano" to understand the requirements. The industry indicated that it in general was very difficult to obtain information about nanomaterials in imported products (nanomaterials and products that contain nanomaterials are typically produced in foreign countries). This type of information is not exchanged in the supply chain and the assessment was that a Danish special legislation is not taken seriously whilst for example the REACH-demands for the documentation regarding especially hazardous substances have global attention.

In general, the project revealed that the Statutory Order is very broad, which is a consequence of nanomaterials being used for many different purposes in many different products and in many different branches. Therefore, potentially thousands of companies have to relate to this Statutory Order [29].

In addition, the project lists a number of suggestions for improvements that include searching the possibilities for a EU-wide solution and a solution with more focus on risk.

Research in EU

EU has invested heavily in research in nano technology. A relatively smaller part of the investments is used for research in nano safety and nano toxicology. This was done, to a certain extent, under the Sixth Framework Programme for Research, Technological Development and Demonstration (FP6) but especially under FP7 and in the current Horizon2020. An overview over FP6 and FP7 projects within nano safety is found at the Nanosafetyclusters homepage (http://www.nanosafetycluster.eu/). EU-financed nano toxicological projects are typically with large budgets at 8-10 million EURO over 3-4 years and with more than 20 partners. The focus is often to create new knowledge within all aspects of nano safety, including physical-chemical characterisation of nanomaterials, development of methods for measurement of exposure for nanomaterials, standardisation of methods for characterisation and measurement of particle exposure, and *in vitro* and *in vivo* studies of potential damaging effects of exposure for nanomaterials dependent on exposure routes. The first projects were typically focussed on developing methods for physical/chemical characterisation and identification of hazards while the subsequent granted projects focus on development of methods and equipment for grouping



There is an extensive political request to make it more visible in which products nanomaterials actually are present and that has been the basis for establishing the Danish nano product register.

The number of reports is up until now is surprisingly low.

and ranking of nanomaterials, development of standard protocols for characterisation and measurement of nanomaterials as well as "control-banding" tools for risk assessment and risk management. Compared to the projects in "Better control of nanomaterials", which usually focussed on surveying and using existing knowledge, these EU research projects are typically research based and are therefore provided with far larger budgets.

Other international fora

OECD: In 2007, the OECD initiated a programme to ensure that nanomaterials are safe for workers and consumers on a global level. The programme was called "OECD Working Party on Manufactured Nanomaterials (WPMN)". The working party has up until today published 61 reports and guidelines e.g. for tests and analyses based on consensus. Under the OECD programme, a test programme that had to investigate to which extent OECD's test guidelines could be used to characterise and test nanomaterials in a satisfactory way, was also launched. This work has resulted in dossiers on 11 industrial nanomaterials. Based on the preliminary activities, OECD regards the existing testing methods as applicable for nanomaterials, however it can be necessary to adapt to specific properties of nanomaterials [39]. OECD has also established a Working Party on Nanotechnology (OECD WPN) that broadly focuses on possibilities for applications of nanomaterials and -technology.

Standardization bodies: In the International Organization for Standardization (ISO), a technical committee for the nano area (ISO TC 229) is established. 35 countries participate actively in the work and 14 countries participate as observers. At the time of this writing, 44 standards and reports regarding nano technology are published.

The European Standardization Committee (CEN) established already in 2006 a technical committee for nano technology (CEN/TC352). The committee coordinates the standardization work initiated in an EU-mandate granted by EU/EFTA. The work is divided in three working groups: WG1) ”Measurement, characterization and performance evaluation”; WG2) "Commercial and other stakeholder aspects"; WG3) "Health, safety and environmental aspects". Up till today, 12 standards regarding the nano technology field from the CEN activities (some in corporation with ISO) are published and many others are in the pipeline.

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Better control of nanomaterials - summary of the 4-year Danish initiative on nanomaterials

Nanomaterials create opportunities for new products but also environmental and health concerns. In 2012, this led the government and its partners to allocate a total of 24 million Danish kroner in the budget to address these concerns. The initiative got the name "Better control of nanomaterials" and the aim was to provide more clarity about the pathways to exposure to nanomaterials and the possible harmful consequences for consumers and the environment. This report disseminates the results of the "Better control of nanomaterials" initiative and provides a summary of the overall conclusions from the 30 reports prepared during the four-year initiative.

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