



Evaluation and control of occupational health risks from nanoparticles

Thomas Schneider et al.

Evaluation and control of occupational health risks from nanoparticles

TemaNord 2007:581

© Nordic Council of Ministers, Copenhagen 2007

ISBN 978-92-893-1563-0

Print: Ekspresen Tryk & Kopicenter

Printed on environmentally friendly paper

This publication can be ordered on www.norden.org/order. Other Nordic publications are available at www.norden.org/publications

Printed in Denmark

Nordic Council of Ministers

Store Strandstræde 18

DK-1255 Copenhagen K

Phone (+45) 3396 0200

Fax (+45) 3396 0202

Nordic Council

Store Strandstræde 18

DK-1255 Copenhagen K

Phone (+45) 3396 0400

Fax (+45) 3311 1870

www.norden.org

Nordic co-operation

Nordic cooperation is one of the world's most extensive forms of regional collaboration, involving Denmark, Finland, Iceland, Norway, Sweden, and three autonomous areas: the Faroe Islands, Greenland, and Åland.

Nordic cooperation has firm traditions in politics, the economy, and culture. It plays an important role in European and international collaboration, and aims at creating a strong Nordic community in a strong Europe.

Nordic cooperation seeks to safeguard Nordic and regional interests and principles in the global community. Common Nordic values help the region solidify its position as one of the world's most innovative and competitive.

Content

Preface	7
Summary	9
1. Introduction	13
1.1 Terminology	14
1.2 The many shapes and structures of nanoparticles	15
1.3 Nanomaterials	16
2. Manufacturing and uses of nanoparticles in the Nordic countries	23
2.1 Introduction	23
2.2 Denmark	23
2.3 Finland	24
2.4 Iceland	29
2.5 Norway	30
2.6 Sweden	33
3. Physical characterization	39
3.1 Introduction	39
3.2 Characterization of pigment grade and ultrafine TiO ₂ and fumed silica	41
3.3 Dustiness of powdered, granular or pelletized nanomaterials	43
4. Assessment of exposure and control measures	49
4.1 Introduction	49
4.2 The COSHH Essentials concept	50
4.3 REACH scenarios	51
4.4 Modelling	52
4.5 Dose	54
4.6 Control approaches	55
4.7 Some specific points	59
5. Workplace exposure data	63
5.1 Introduction	63
5.2 Ultrafine particles	64
5.3 Engineered nanoparticles	67
5.4 Background concentration	68
6. Specific exposure scenarios	69
6.1 Introduction	69
6.2 Welding	69
6.3 Exposure to amorphous SiO ₂ fume in smelters	70
6.4 Paint manufacturing	71
6.5 Paint and lacquer sanding	71
6.6 Textile manufacturing	72
6.7 Spraying (surface treatments)	73
6.8 Nanoscale surface coating	74
6.9 Production of metal oxide nanoparticles (laboratory scale)	74
6.10 Handling of carbon nanotubes	75
6.11 Laboratory handling of nanopowders	75
6.12 Failure testing and demolition of carbon nanotube-doped concrete	75
6.13 Ski waxing	77
6.14 “Consumers” exposed to sprays	78
7. Occupational exposure during entire life cycle	81
8. Quality of information in MSDS	83

8.1 Introduction.....	83
8.2 The MSDS	84
8.3 Results in brief	84
8.4 Discussion.....	85
9. Trends in uses of nanoparticles	87
References.....	89
Resume	93

Preface

Rapid growth in the nanoparticle industry is anticipated in the Nordic countries owing to highly focused national research and investment initiatives. This technological development should not compromise health and safety of workers and the general public, but national research initiatives are lagging behind. All Nordic countries have targeted research and development programs on nanoparticles, nanosurfaces and nanostructures in industry or at universities and other research laboratories. Only a minor part of this research addresses health risks.

This report presents data for evaluation and control of occupational health risks from nanoparticles that has been obtained in the Nordic Council of Ministers project No. 411050-60091. Focus has been on exposure by inhalation. Working environment researchers from all Nordic countries have worked together to produce this report. The contributors have been

Thomas Schneider, National Research Centre for the Working Environment, Copenhagen. Editor

Anders Jansson, Department of Applied Environmental Science, Stockholm University

Keld Alstrup Jensen, National Research Centre for the Working Environment, Copenhagen

Vidur Kristjánsson, Administration of Occupational Safety and Health, Reykjavik

Marita Luotamo, Finnish Institute of Occupational Health, Helsinki

Olle Nygren, National Institute for Working Life, Umeå

Kai Savolainen, Finnish Institute of Occupational Health, Helsinki

Vidar Skaug, National Institute of Occupational health, Oslo

Yngvar Thomassen, National Institute of Occupational health, Oslo

Antti Tossavainen, Finnish Institute of Occupational Health, Helsinki

Timo Tuomi, Finnish Institute of Occupational Health, Helsinki

Håkan Wallin, National Research Centre for the Working Environment, Copenhagen

Thomas Schneider

Copenhagen, July 2007

Summary

Applications of engineered nanoparticles are expected to enable huge economic and technological possibilities. Some of these special properties, in particular reactivity, have raised concerns regarding human health. Due to these concerns scientists, regulators, and the industry have initiated efforts to gain knowledge about worker exposure and to define safe uses of the different engineered nanoparticles.

The report presents a general overview of nanoparticles and the industrial production and uses of nanoparticles in the Nordic countries. A distinction is made between

- Engineered nanoparticles, i.e. particles having a diameter between 1 and 100 nm and intentionally engineered and produced with specific properties, including shape, size, surface properties, and chemistry and
- Ultrafine particles, a term that has been used to describe airborne particles smaller than 100 nm. The term “ultrafine” has been in existence longer than “nano”. The term is frequently used for particles that have not been intentionally produced but are incidental products of processes such as combustion and welding. Also several intentionally produced particles with primary particle sizes in the nanosize range (e.g. carbon black, silica fume, and titanium dioxide TiO_2) are often called “ultrafine”.

A range of material technologies involve processes that transform conventional materials into nanosized particles. As an example thermal surface coating by e.g. plasma spraying applies nanoparticles to obtain coatings with nanoproperties. Significant number concentrations of nanosized particles are also generated as by-products of conventional processes that involve evaporation/condensation. Welding and laser ablation are such processes.

Engineered nanoparticles include metallic and ceramic nanoparticles, Fullerenes, one of the most well-known nanoparticles, nanotubes, of which the most well-known are the carbon nanotubes, nanofibres, nanoclays, nanocapsules, dendrimers, quantum dots, and nanoclusters. Some high-lights of research, manufacturing, and use of nanoparticles in each Nordic country are presented.

Both granulometry (size distribution) of the powder as is and the ability of the powder to generate airborne dust (dustiness) when handled are essential data for use in risk assessment both for new and existing substances. Annex V of Dir 67/548/EEC does not yet sufficiently cover these testing requirements. In the absence of formal requirements, the project

group has proposed that a first step physical characterization should include particle size, particle morphology, agglomeration state, specific surface area, crystallinity, and elemental composition. Three powders

- an uncoated anatase titanium dioxide pigment
- an alumina treated ultrafine rutile titanium dioxide
- dry silica fume

were characterized according to this scheme. As an example the surface areas were $5.5 \text{ m}^2 \text{ g}^{-1}$ for titanium dioxide pigment, $112 \text{ m}^2 \text{ g}^{-1}$ for ultrafine rutile titanium dioxide, and $12 \text{ m}^2 \text{ g}^{-1}$ for silica fume.

The very few existing dustiness tests have shown that handling of nano-sized powders tend to generate particles with a size mode below $1 \mu\text{m}$, typically $100\text{--}300 \text{ nm}$, and one or several size modes above $1 \mu\text{m}$. Carbon nanotube powders have been found to generate low number concentrations.

To further explore dustiness, a new dustiness test was developed that used minimal amount of material and that in a simple manner could bridge the two test principles given in the EN 15051 standard for dustiness testing. Tests were performed for the powders ultrafine and pigment grade TiO_2 , fumed silica, bentonite, yttrium stabilized zirconia, goethite, two grades of corundum (aloxite F800 and F1200), and talc. All materials generated dust having two size modes above $0.9 \mu\text{m}$. All materials except pigment grade TiO_2 and aloxite F1200, also generated a size mode in the range from ~ 100 to $\sim 220 \text{ nm}$. TiO_2 pigment grade had the lowest dustiness and TiO_2 ultrafine the highest dustiness as measured by particle number for both the single drop and rotation test and as measured by mass for both tests combined. The difference was a factor of ~ 300 . A similar large difference in exposure potential can be expected. This would imply that preventive measures would have to be much stricter if pigment grade TiO_2 were to be replaced by the ultrafine version. Since aggregates of ultrafine TiO_2 can brake up in the lung fluid and assuming particle number matters, the potential risk would even be larger. The results indicated also that when handling nanosized powders, the generated airborne particles are not single nanoparticles but agglomerates.

There is a wide gap in information on the risks to specify which levels of control are required and thus to provide guidance on choice of proper control measures. However, several approaches developed for conventional materials provide a conceptual framework for describing and analysing exposure scenarios and specific control approaches for nanomaterials. These include control banding and exposure modelling. These concepts are described. The project group is of the opinion that the engineering control techniques of nanoparticle exposure can build on the knowledge and experience from current exposure control of aerosols which already today has been applied to aerosols containing ultrafine

particles such as e.g. welding fume, carbon black, or viruses. Effective techniques can be obtained by adaptation and redesign of current technology. This applies to techniques for general ventilation, industrial ventilation, local and process ventilation, containments and enclosures, and filtration.

Also occupational hygiene assessment of workplaces can follow existing methods. One exception is that even extremely high concentrations of nanoparticles may not be visible to the naked eye, and thus sensitive particle detectors, such as condensation particles may have to be used.

There are currently no national or international consensus standards on measurement techniques for nanoparticles at the work place. This has constrained generation of exposure data and existing data on occupational exposure to engineered nanoparticles are very limited. Monitoring exposure by inhalation to nanoparticles presents some unique challenges. Most exposures will be in the form of aggregates. No simple measurement approach is at hand for assessing the degree of agglomeration of airborne particles and the potential break up into many smaller units in the lung fluids after inhalation

High background concentrations of ultrafine particles are ubiquitous. At present there are only two approaches available for separating between engineered nanoparticles and background particles of the same size range for use outside the research laboratories. One is by intelligent design of sampling strategies. The other is to collect particles on suitable substrates for later analysis in the laboratory using time consuming electron microscopy.

In order to put exposure to engineered nanoparticles into perspective, exposures to ultrafine particles for some selected scenarios is presented. Particle number concentrations can range from over 10 000 000 particles cm^{-3} for laser welding to concentrations of the order 1 000 to 10 000 particles cm^{-3} for bagging ultrafine powders.

One aim of the project was to collect examples of specific engineered nanoparticle exposure scenarios. However, very few scenarios were available for study, an experience also gained by colleagues in other European countries. The presented data for characterizing exposure scenarios is thus variable and limited in extent. General conclusions regarding exposure risk thus cannot be drawn.

Due to lack of existing information, the project group could not meaningfully assign likelihood and intensity of occupational nanoparticle exposure for representative exposure scenarios during a life cycle.

The quality of information provided in Material Safety Data Sheets for nanoparticles was investigated. Materials were chosen with primary particle sizes as small as possible, to reflect a range of properties. The materials categories (number) were: silica (8), titanium dioxide (4), zirconium dioxide (2), carbon nanotubes (11), C_{60} Fullerenes (2), and cadmium-based quantum dots (3).

In general the identification of the substance and the identification of the company were satisfying. Within the groups there was inconsistency in listing of R-phrases. Classification and labelling were many times missing from the MSDS, because there were no test results available for the substance or compound in question. In some cases “nano” was indicated in the commercial name of the material. Most of the carbon nanotube materials were identified as graphite.

The quality of the proposed handling, storage and exposure controls varied much between the MSDS even for materials of the same character. Also the descriptions of physical and chemical properties, conditions and materials to avoid were very different between the MSDS. Some MSDS had well described lists of exposure limit values and toxicity tests. Even for similar materials however the described toxicological properties varied. There was very little ecological information in the MSDS.

In general the compounds/materials were practically not tested, and if so, many times for acute toxicity only.

Finally, some information on future trends in production and uses of nanoparticles is presented.

1. Introduction

Engineered nanoparticles have attained marked attention due to their revolutionary properties. Applications of engineered nanoparticles are expected to enable huge economic and technological possibilities. Some of these special properties, in particular reactivity, have raised concerns regarding human health. Due to these concerns scientists, regulators, and the industry have initiated efforts to gain knowledge about worker exposure and to define safe uses of the different engineered nanoparticles.

This report begins with a general overview of nanoparticles and the industrial production and uses of nanoparticles in the Nordic countries. The risk of inhalation exposure to potentially highly toxic or high-volume engineered nanoparticles with potentially wide ranges of application during production and industrial is characterized based on a very limited set of specific exposure scenarios. Contrary to the expectations at the outset of the project, only few industries in the Nordic countries were available for that part of the study. The results of an investigation into the quality of information provided in Material Safety Data Sheets for nanoparticles are reported and the need for revision of safety information is identified. Finally, some information on future trends in production and uses of nanoparticles is presented.

The role of dermal exposure is unclear. It is very likely that systemic exposure will be much less via the dermal than via the inhalation route (Hoet *et al.*, 2004). For local effects little is known whether size in addition to composition is a risk determinant. Dermal exposure thus has not been considered in this report.

The project group decided to not either include the following nano-particles in the report:

- Nanoparticles for pharmaceutical and medical purposes
- Use of nanoparticles in the food container industry because this is subject to special regulation
- Nanoparticles used or generated in relation to electronic chip manufacturing because workers are well protected in this industry with its production-induced extreme requirements on “particle-free” air.

1.1 Terminology

In this report, the following terms and definitions have been adopted based on NIOSH (2007), SCENIHR (2007), and others:

- *Nanoscale*. Having one or more dimensions of the order of 100 nm or less.
- *Nanomaterial*. Material with one or more external dimensions, or an internal structure of 100 nm or less, which could exhibit novel characteristics compared to the same material without nanoscale features.
- *Nanoparticle*. Particles having a diameter between 1 and 100 nm. Nanoparticles may be suspended in a gas (as a nanoaerosol), suspended in a liquid (as a colloid or nanohydrosol) or embedded in a matrix (as a nanocomposite). The precise definition of particle diameter depends on particle shape as well as how the diameter is measured. For instance, carbon fullerenes represent nanoparticles with identical dimensions in all directions (spherical), whereas single-walled carbon nanotubes (SWCNTs) typically form convoluted, fibre-like nanoparticles with a diameter below 100 nm.
- *Nanocomposite*. Composite in which at least one of the phases has at least one dimension on the nanoscale.
- *Nanotechnology*. The manipulation of matter on a near-atomic scale to produce new structures, materials, and devices.
- *Agglomerate*. A group of particles held together by relatively weak forces, including van der Waal forces, electrostatic forces and surface tension.
- *Aggregate*. A group of particles bonded together by relatively strong forces and thus not easily broken apart.
- *Engineered nanoparticle*. A nanoparticle intentionally engineered and produced with specific properties, including shape, size, surface properties, and chemistry.
- *Ultrafine particle*. This term has been used to describe airborne particles smaller than 100 nm. The term “ultrafine” has been in existence longer than “nano”. The term is frequently used for particles that have not been intentionally produced but are incidental products of processes involving combustion, welding, or diesel engines. Also several intentionally-produced particles with primary particle sizes in the nanosize range (e.g. TiO₂) are often called “ultrafine”.
- *Nanoaerosol*. A collection of nanoparticles suspended in a gas. The particles may be present as discrete nanoparticles, or as assemblies (aggregates or agglomerates) of nanoparticles. These assemblies may have diameters larger than 100 nm. In the case of an aerosol consisting of micrometer-diameter particles formed as agglomerates of nanoparticles, the definition of nanoaerosol is open to interpretation. It is generally accepted that if the nanostructure associated with the nano-

particles is accessible (through physical, chemical, or biological interactions), then the aerosol may be considered a nanoaerosol. However, if the nanostructure within individual micrometer-diameter particles does not directly influence particle behaviour (for instance, if the nanoparticles were inaccessibly embedded in a solid matrix), the aerosol would not be considered a nanoaerosol.

- *Colloids.* A colloid consists of two separate phases: a dispersed phase and a continuous phase. The dispersed phase is made of tiny particles or droplets that are distributed evenly throughout the continuous phase. The size of the dispersed phase particles are between 1 nm and 1000 nm in at least one dimension. Homogeneous mixtures with a dispersed phase in this size range may be called colloidal aerosols, colloidal emulsions, colloidal foams, or colloidal dispersions.

1.2 The many shapes and structures of nanoparticles

Specification of particle size in nanomaterials is often given in terms of particle size or specific surface area or both. For spherical particles the specific surface area, A , is given by

$$A = 6/(d\rho) \text{ [cm}^2 \text{ g}^{-1}\text{]}$$

where d is diameter [cm] and ρ density [g cm⁻³]. For unit density particles the values in Table 1 are obtained.

Table 1. Small in size, large in number and surface

Size, nm	Specific surface area, m ² g ⁻¹	Mass concentration, µg m ⁻³	Number concentration, cm ⁻³	Surface concentration, m ² m ⁻³
5	1200	1	15 000 000	12
50	120	1	15 000	1.2
500	12	1	15	0.12
5000	1.2	1	0.015	0.012

There are different approaches for classification of nanoparticles. Table 2 reproduces a proposal given in Luther (2004).

Geometrical particle structure is not an invariant. Some nanoparticle based powders may be designed to contain aggregates of primary nanoparticles, while others are purposely coated to prevent agglomeration. Nanoparticles may agglomerate when collected in bulk, and they may de-agglomerate following mechanical impact. It has been hypothesized (Maynard, 2002) that some manufacturing processes lead to the formation of primary aggregates (defined as clusters of primary particles held together by partial sintering) that represent the limit of de-agglomeration.

Table 2. Classification of nanomaterials according to Luther (2004).

Classification	Examples
<i>Dimension</i>	
3 dim < 100 nm	Particles, quantum dots, hollow spheres
2 dim < 100 nm	Tubes, wires, platelets
1 dim < 100 nm	Films, coatings, multi-layer
<i>Phase composition</i>	
Single-phase solid	Crystalline, amorphous particles, layers
Multi-phase solid	Matrix composites, coated particles
Multi-phase system	Colloids, aerogels, ferrofluids
<i>Manufacturing process</i>	
Gas phase reaction	Flame synthesis, condensation, CVD
Liquid phase react.	Sol-gel. Precipitation, hydrothermal
Mechanical	Ball milling, plastic deformation

Engineered nanoparticles can be manufactured with different coating to obtain specific properties, and this could potentially affect toxicological properties. As an example, TiO₂ in sunscreens are coated to suppress the radical formation by photocatalytic action (Moloney *et al.*, 2002). This is a further example illustrating the diversity and complexity of nanoparticle based materials, and thereby the challenges in their proper characterization for health risk assessment.

1.3 Nanomaterials

Particles in the nanosize range have been generated in vast amounts by established technologies, such as paint pigments, carbon black and silica fume. Such intentionally-produced particles with primary particle sizes in the nanosize range are often called “ultrafine”. Manufacturing of ultrafine TiO₂ started in the 1990’ies (Hext *et al.*, 2005). Nanomaterials also include materials manufactured by new methods designed to reduce or better control size relative to the conventional product.

1.3.1 Carbon Black

Carbon blacks are manufactured by thermal oxidative dissociation of hydrocarbons such as mineral oils or natural gases. They consist of elemental carbon, but there is a wide variety of products available, dependent on the starting materials and method of manufacture. The primary particle size ranges from around 10 nm and upwards.

Carbon blacks are classified according to an internationally recognised system, which signifies the manufacturing process and the jetness (degree of blackness).

- Channel blacks are produced by burning petroleum gases in an atmosphere deficient in oxygen. This process is not very used because it has disastrous consequences on the environment.

- Furnace blacks are produced by the thermal oxidative process in which hydrocarbon oils are burned in a limited supply of air.

The rubber industry is by far the biggest user of carbon blacks. In comparison, the paint industry is only a modest user. The printing inks industry also uses significant quantities. Finer particle blacks are used for high-quality finishes such as in automotive paints on account of their higher jetness. Medium size blacks are used for intermediate quality paints, whereas the coarser pigments are used for decorative paints.

1.3.2 Silica fumes (SiO_2)

Silica fumes (SiO_2) is a by-product of the reduction of high-purity quartz during the production of silicon metal or ferrosilicon alloys. The fume, which is condensed from gases escaping from the furnaces, has a very high content of amorphous silicon dioxide (> 99 %), and is made of spherical particles with typical median particle size of 120-150 nm. Originally, it was considered a waste. In Norway recovery began in the 1960's (Elkem Materials, 2007). To meet present demands, silica fume is produced on purpose worldwide.

1.3.3 TiO_2

The production process for nano TiO_2 is cool vaporization while normal TiO_2 is produced chemically by the sulphate or the chloride process. Nano TiO_2 has a particle size typically of less than 100 nm, while normal TiO_2 used as a paint pigment has a median particle size of approx. 300 nm.

As the size of the particles reduces to the nanometre scale, new photochemical characteristics occur in the particles. For example, the rutile nano TiO_2 particle can block UV light while visible light can pass through. On the other hand, anatase nano TiO_2 may have a strong photocatalytic effect. Supplied with energy by UV-light, electron-cavities can emerge on the surface of the particle, which can oxidize big organic molecules attached to the particle. Therefore, nano TiO_2 is applicable in such fields as UV-block sunscreen, UV-block paint, environmental treatment, and in liquids for treatment of transparent wood surfaces. It is also used for self-cleaning material, as an anti-microbial agent, and thus being used in a broad range of traditional industries.

1.3.4 Consumer products

Nanoscale materials are used in consumer products including electronic, cosmetic, automotive, and medical products. It is difficult to determine how many "nano" consumer products are on the market and which merchandise could be called "nano". The Woodrow Wilson International

Centre for Scholars (2007) has published an inventory that gives the public the best available look at the 450+ nanotechnology-based consumer products currently on the market.

1.3.5 Technologies based on nanoparticles

A range of material technologies involve processes that transform conventional materials into nanosized particles. As an example thermal surface coating by e.g. plasma spraying applies nanoparticles to obtain coatings with nanoproperties.

1.3.6 Unintentional production

Significant number concentrations of nanosized particles are generated as by-products of conventional processes that involve evaporation/condensation. Welding and laser ablation are such processes. The trend in welding techniques causes the generated fume particles to become ever smaller. Also use of metal working fluids can generate considerable number concentrations of nanosized particles (Peters *et al.*, 2006). Combustion processes (e.g. in diesel engines and gas burners) are significant sources of nanosized particles (Kuhlbusch *et al.*, 2004; Kuhlbusch and Fissan, 2006).

1.3.7 Engineered nanoparticles

A broad range of engineered nanoparticles are manufactured on industrial, pilot, or experimental scales.

Metallic and ceramic nanoparticles. Metallic nanoparticles consist of single metals while the ceramic nanoparticles include metal oxides, silicates, carbides etc. Examples of metal oxides are e.g. pigment (TiO_2 , ZnO , Fe_2O_3), sunscreen (TiO_2), magnetic storage media (Fe_2O_3), fillers, coatings, catalysts. The clay mineral montmorillonite ($\text{Ca}_{0.5}\text{Na}_{0.7}(\text{Al,Mg})_4[(\text{Si,Al})_8\text{O}_{20}]\cdot n\text{H}_2\text{O}$) is an example of a nanosilicate.

Fullerenes. Fullerenes are one of the most well-known nanoparticles. They are hollow constructs of pentagon and hexagon units of carbon atoms. The first to be described was buckminsterfullerene C-60, named after the architect Buckminster Fuller (Figure 1). Since its discovery in 1985, larger spherical fullerenes have been produced, such as C-70, C-76, C-78 and C-84, and closed tubes based on the fullerene structure.

Examples of use: catalysis, pyrolysis, fillers in e.g. tires and building materials, lubricants, solar cells, electrolytic membranes and proton-exchange membranes in fuel cells, oxygen and methane storage materials, drug delivery.

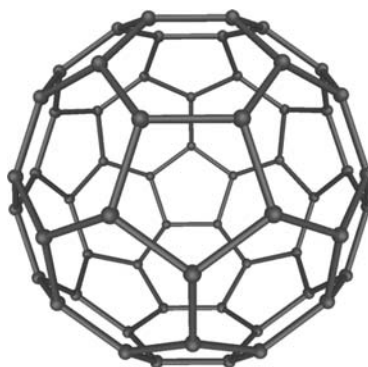


Figure 1. Buckminsterfullerene, C-60

Nanotubes. The most well-known nanotubes are the carbon nanotubes (CNT) being different variations over the fullerene structure. Nanotubes can also be made of boron-nitride, cyclic peptides and proteins. Nanotubes are produced as long, short, single walled (SWNT), multi walled (MWNT), open, closed, spiral shaped, etc. CNT's have a tensile strength more than 100 times that of steel, are better thermal conductors than diamonds, and their electrical conductivity equals that of copper. The theoretical lower diameter limit for SWNT is 0.4 nm, while the typical diameter is 1.2 nm. MWNT have larger diameters, such as about 10 nm for 8-15 walled MWNT (Figure 2).

Examples of use: electron field emitters, hydrogen storage in fuel cells, chemical sensors, biosensors, electromagnetic shielding, super capacitors, lighting technology, polymer composites, fillers, super strong cables, lightweight parts for cars, planes, and space vehicles, and textiles.

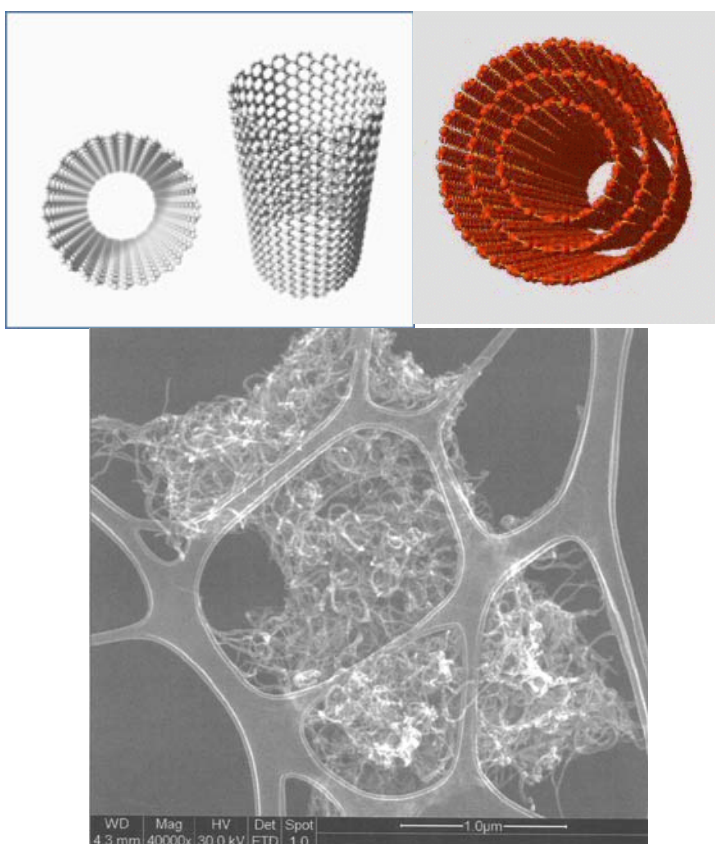


Figure 2. Single-walled (top left) and multi-walled (top right) carbon nanotube structures. Multiwalled carbon nanotubes (bottom). Bar length 1000 nm.

Nanofibres. Carbon nanofibres can be either hollow or massive. Their length is typically a few micrometers, and with range from 10 nm to 200 nm. Carbon nanofibres differ from carbon nanotubes by not having a penetrative ordered fullerene structure. Nanofibres can also be made of a wide variety of polymeric materials and with a broad range of chemical composition and fibre diameter and length. Nanofibres made of cellulose polymers or polyurethane can be used for drug delivery. Carbon nanofibres are produced in large scale in the USA and the Far East.

Examples of use: drug delivery, filler in technical and construction material, super-strong cables, light-weight automotive parts, and textiles.

Nanoclays. Nanostructured organically modified layer silicates have been used for some time as fillers in polymers, as flame-retardants, and as mechanical reinforcement. They are also used to decrease gas diffusion through foils for packaging and for tennis balls. If used in material for car tyres they may be used in large quantities.

Nanocapsules. Nanocapsules are defined as a nanoparticle that consists of a shell and a cavity. The desired substance can be placed in the cavity. Previously, nanocapsules usually consisted of organic substances - phospholipids (the same substance our cell walls are made of) and liposomes (fatty tissue), but are increasingly produced from synthetic poly-

mers. Nanocapsules have been produced for many years for medical application.

Examples of use: medical application, drug delivery.

Dendrimers. Dendrimers are controlled-structure multi-branched polymers with nanoscale dimensions. They can display both hydrophilic and hydrophobic characteristics and can accommodate a wide variety of functional groups for medical applications. They are expected to be used in the medical and biomedical field.

Quantum dots and nanoclusters. These materials represent high volume or soon-to-be high volume materials. Very small metallic nanoparticles can also be classified as quantum dots. Normally, quantum dots are inorganic nanocrystals with specific fluorescing, magnetic or electrical properties. There are two types on the market: core dots or core-shell dots. Core dots consist e.g. of CdSe and PbSe, while CdSe/ZnS, CdTe/CdS, HgSe/Fe, and InAs/GaAs are examples of core-shell dots. The slash distinguishes the composition of core and shell. Quantum dots can be made from most semiconductors and pure metals (e.g. Au, Ag, Ni, Co). Quantum tubes and quantum wires are under development.

Examples of use: medical and biological image analysis, energy conversion in solar cells, semiconductor technology, catalysts, magnetic storage.

2. Manufacturing and uses of nanoparticles in the Nordic countries

2.1 Introduction

This section presents some high-lights of manufacturing and use of nanoparticles in the Nordic countries and does not intend to be comprehensive.

2.2 Denmark

More than 50 enterprises are in the process of developing or establishing production based on nanotechnology. Nanomaterials with new functional properties is one of seven prioritized R&D areas in Denmark (Danish Ministry of Research, Technology, and Development, 2004). Large companies, being international leaders in their respective fields are already using nanotechnology. These industries are food, product ingredients, measuring equipment, catalysis, medicine, medico-technology, and advanced engineering and electronics.

An inventory has been made of consumer products on the Danish market that contain nanoparticles or are based on nanotechnology (Stuer-Lauridsen *et al.*, 2007). With the exception of the Association of Danish Cosmetics, Toiletries, Soap and Detergent Industries in Denmark other trade associations (textiles, paint and lacquer, chemical products) reported, that there is still limited activity regarding production, formulation or import of such consumer products. 243 consumer products were identified and were mainly from the surface treatment, cosmetics, and sports gear markets. 154 of the products were for surface treatment. It had only for 41 of the products been possible to identify the nanomaterial used: cosmetics (zinc oxide 6, titanium dioxide 13, antibacterial silver (textiles and household machines 10), CNT (sports gear 7), and Fullerenes (cosmetics 5). A corresponding inventory on industrial production and use in Denmark is ongoing.

Haldor Topsoe A/S is a leading manufacturer of catalysts. According to Haldor Topsoe (2007) catalysts are today the most important group of commercial nanomaterials. They will continue to be an important area of nanotechnology enabling solutions to many important resource, energy and environmental problems by tailor-made nanostructured catalysts.

The Danish High Technology Fund supports a major four-year project aimed at developing "nano-nonwovens". The project is carried out jointly by the only Danish nonwovens manufacturer, Fibertex A/S based in Aalborg, and the iNANO centre (Interdisciplinary Nanoscience Centre) based at the University of Aarhus and Aalborg University (Fibertex, 2005). The goal is to employ nanoparticles into so-called nonwovens, which are used for a wide range of purposes such as raw materials for diapers, the furniture and bedding industry, the automotive industry as well as for geotextiles for use in road and harbour construction. The high-technology project will utilise nanotechnology and nanoparticles to give the nonwovens new and unique properties that open entirely new applications. Examples are use of nanoparticles to improve the mechanical and functional properties of the fibres to produce environmentally friendly and fire-retardant materials.

NanoCover Scandinavia is a Danish company established in 2005. It develops and produces a series of products for surface treatment using nanoparticles and other nanotechnologies.

2.3 Finland

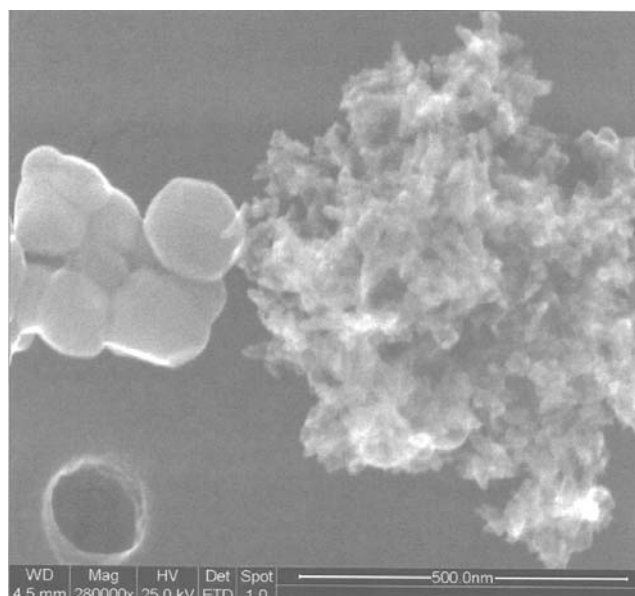
The Finnish Institute of Occupational Health, FIOH, has been very active in nanotechnology and related research projects within the last few years. FIOH participates in the NANOSH EU-project as well as the national NANOHEALTH project within the national Finnish Academy funded research-program. Nanotechnology is a very active industrial sector in Finland with more than 100 companies involved in nanotechnology. However, there is still a limited amount of commercial application in Finnish nanotechnology industry. In the report "Nanotechnology in Finnish Industry" by Spinverse Consulting Oy, the applications and stages of development shown in Figure 3 were identified. This report will be updated later in 2007.

The next sections present a few examples of already existing products and/or strong research activities in Finnish nanotechnology.

Kemira Oy is a premier supplier of TiO_2 pigments that provide the best opacity and dispersion for packaging inks, decorative paints and industrial coatings, as well as plastics and paper applications (Figure 4 left, Figure 5 left). The AFDC product range comprises white, opaque, and extra pure Kemira specialty TiO_2 for food, drugs and cosmetics applications. Kemira supplies also a UV-TITAN product range comprising several grades of ultrafine, transparent rutile TiO_2 used in cosmetics, plastics and coatings applications (Figure 4 right, Figure 5 right).

Nanotechnology Applications Can Be Found in All Stages of Development and All Industries...				
	Applied research	Product development	Early commercialization	Established business
Electronics	<ul style="list-style-type: none"> New design and packaging methods for nanoelectronics 	<ul style="list-style-type: none"> Battery technologies New sensors Electronics packaging Printable electronics 	<ul style="list-style-type: none"> Enhanced optical fibres New laser technologies 	<ul style="list-style-type: none"> Coatings, e.g. ALD Lasers Diffraction optics Sensors: gas, inertial
Medical/Biotech	<ul style="list-style-type: none"> Nanocoatings in plastics Biosensors 	<ul style="list-style-type: none"> Biosensors Nanoparticles in diagnostics DNA-chips 	<ul style="list-style-type: none"> Diagnostics systems, multi/self-testers Enzymes and reagents 	
Chemical	<ul style="list-style-type: none"> Process efficiency improvements Sulphur extraction with enzymes 	<ul style="list-style-type: none"> Co and Ni nanopowders 6n pure metals Nanocomposites 	<ul style="list-style-type: none"> Nanofilms in filtering Catalysts UV shielding in paints 	<ul style="list-style-type: none"> TiO₂ Conducting polymers
Forestry	<ul style="list-style-type: none"> Intelligent packaging, sensors 	<ul style="list-style-type: none"> Multicoating/tailored papers, cartonboard Multi-layer laminates Nanofilters 	<ul style="list-style-type: none"> Functional polymers 	
Metal	<ul style="list-style-type: none"> Ceramic composites to replace metals 	<ul style="list-style-type: none"> Self-cleaning and scratch-proof metal coatings 	<ul style="list-style-type: none"> Carbon coatings 	
Other	<ul style="list-style-type: none"> Nanocoatings in plastics ESD-textiles 	<ul style="list-style-type: none"> Ceramics Nanocomposites in packaging Nanofibres for air filters 	<ul style="list-style-type: none"> Water cleaning 	<ul style="list-style-type: none"> Nanocoatings in glass Nanoparticles & UV filtering in cosmetics Catalysts for cars

Figure 3. Nanotechnology in Finnish Industry.

Figure 4. SEM image of AFDC range TiO₂-pigment (left) and UV-TITAN range ultrafine TiO₂ (right), measure bar is 500nm.

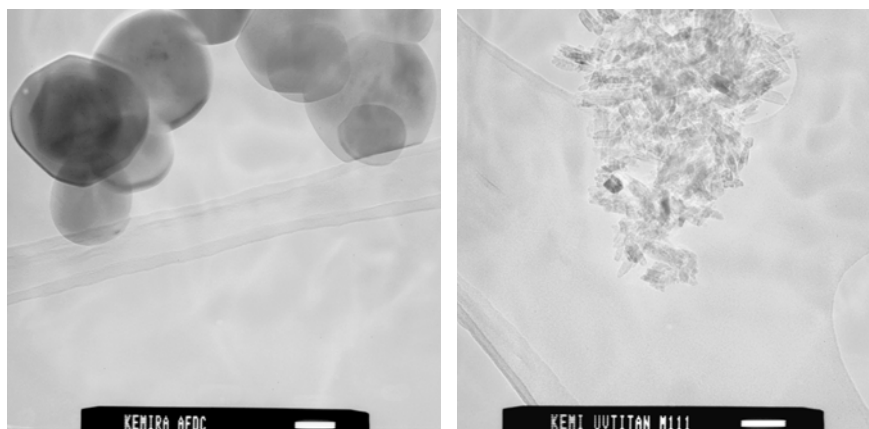


Figure 5. TEM images on AFDC range TiO_2 -pigment (left) with average particle size of 170nm and UV-TITAN range ultrafine TiO_2 (right) with average particle size of 4 nm, measure bar in the images is 50 nm.

Montreal Sports Oy manufactures advanced hockey sticks for professional and amateur players. They use low-cost carbon nanotubes, CNT, in epoxy matrix (Figure 6) in large quantities. Amroy Europe Inc. (Finland) is responsible for development of the CNT-epoxy resin.

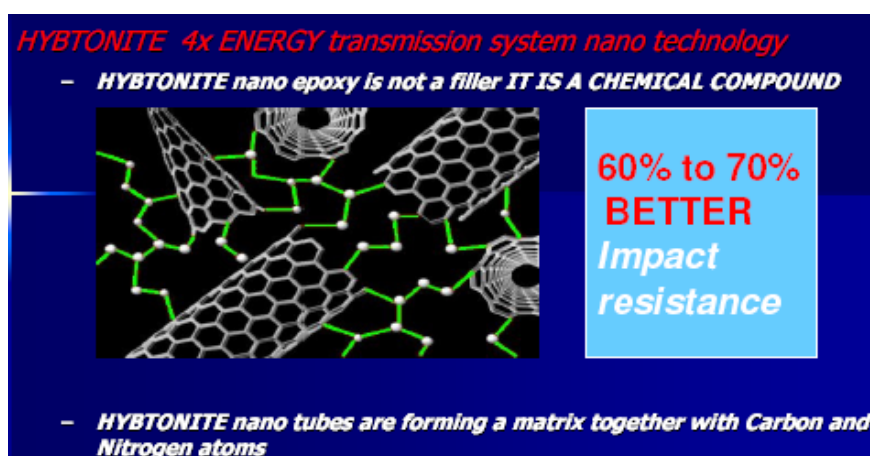


Figure 6. The basic idea of Hyptonite nano epoxy material (From Antti Valtakari, presentation at Nanotech Northern Europe conference in March 2007, Helsinki).

The Ecocat company is focused on the development and production of substrates and catalytic converters for petrol and diesel vehicles, small engines, aftermarkets and industrial applications. Ecocat manages the whole process from designing and manufacturing the substrate to active coatings and the assembly of the catalyst or the filters. In addition to ready-coated catalyst solutions, Ecocat also delivers substrates for customers to be coated. Washcoat characteristics play a major role in conversion efficiency. By modifying the washcoat, catalyst selectivity can be adjusted based on requirements and raw emissions. This enables maximum conversions with minimum use of precious metals. The functioning

of catalytic coatings is based on reactions of precious metals (platinum, palladium, and rhodium) with emissions (Figure 7). As an outcome, carbon monoxide CO and hydrocarbons HC oxidise into CO₂ and water while reducing NO_x to nitrogen. Ecocat has fitted the catalytic coatings into three-way, oxidation, and deNO_x catalysts for different types of engines, fuels and emission limits. Besides diesel, petrol, gas and bio-fuel, Ecocat has tailored its own coating solution for small engines.

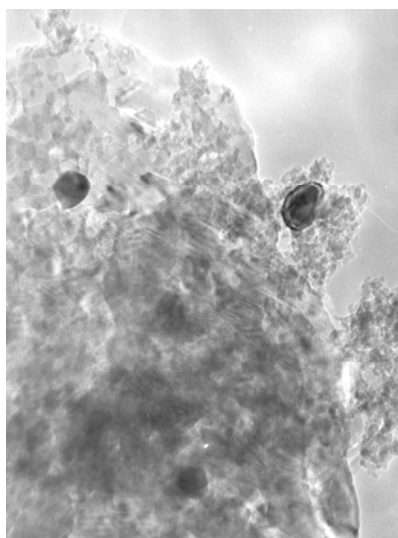


Figure 7 TEM-image of air-aged (1000°C) catalyst model material: gamma-alumina washcoat powder with palladium particles (Image taken by M.Vippola).

At Tampere University of Technology there has already for years been active research on developing the manufacturing process for nanopowders with liquid flame spray method. In the LFS process, the liquid precursor is atomized into micron-sized droplets, which are introduced into a turbulent H₂–O₂ flame. Evaporation of the liquid solvent droplets in the flame, followed by decomposition and re-condensation of product species, finally generates a well-defined, nearly monodisperse nanoparticle material, to be sprayed on a surface or to be collected (Figure 8 and 9). In the process the liquid precursor is fed into the spray gun atomizer with a manually controlled infusion pump. A certain mass flow of precursor can be achieved with several combinations of precursor concentration in liquid and liquid feed rate. For producing multicomponent nanoparticles from micron-sized precursor droplets using LFS, in the ideal case, most of the material should be vaporized and, subsequently (either directly or via chemical reactions), nucleated and re-condensed. With this method various different nanopowders can be produced, such as Al₂O₃, TiO₂, Ag-Pd, Fe₂O₃, Ag, Pd, and ZrO₂. This same LFS process with different modifications is used also in some Finnish nanotechnology companies: Beneq

Oy uses it mainly for applying functional coatings on glass and ceramic tiles. It is also used for multi-component nanoparticle synthesis. Liekki instead has developed a fibre production technology, Direct Nanoparticle Deposition (DND). The DND technology deposits directly and simultaneously nanometre sized particles containing both the waveguiding elements and the active ions. This technology avoids the slow and limited process of conventional solution doping. DND technology enables production of state-of-the-art highly doped fibres that minimize required fibre length, provide strong amplification with broad and flat gain profile, have high efficiency and excellent beam quality as well as reduced photo-darkening and reduced nonlinear effects. Nanoparticle doped fibres have very good usability in terms of splicing properties, temperature and bending characteristics.



Figure 8. Picture taken from the LFS process while producing ZrO_2 nanopowder.

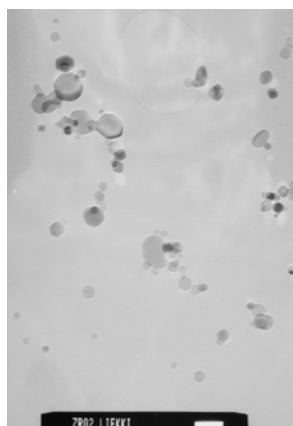


Figure 9. TEM-image of ZrO_2 nanopowder, measure bar in TEM-image is 50 nm.

Nanoharju is a cluster of Finnish companies using nanotechnology. The companies are particularly experienced in the manufacturing, use and characterisation of nanomaterials and products utilizing these materials. The products that these companies provide include e.g. Atomic Layer Deposition (ALD) equipment and process know-how, real-time particle measurement equipment, industrial equipment for the production of nanomaterials (including nanocoatings), high-purity chemicals as well as high-power active fibres for fibre lasers.¹

2.4 Iceland

The Icelandic Alloys Ltd (Íslenska járnblendifélagið EHF) has since 1978 produced ferrosilicon. The production is now about 105 000 tonnes per year. The gases from the furnaces are led through cooling towers and then through a filter system where silicon dioxide dust (SiO_2) is collected. The first years the dust was treated as waste. In the late 1980'ies the Icelandic Cement Production Plant (Sementsverksmiðja ríkisins) started to mix SiO_2 to the cement to control the pH-value. Later it has been used to strengthen the concrete. Now all the SiO_2 produced as by-product is used, a small part in Iceland but most of it is exported. The amount that is produced as by-product is about 18 000 tonnes per year.

• ¹ <http://www.nanoharju.fi/>

2.5 Norway

2.5.1 Engineered nanomaterials

In 2002, the Norwegian Research Council made nanomaterials and nanotechnology a priority through the NANOMAT programme. The project is one of the three foresight programmes recently undertaken by the Research Council to enhance the expertise in some of the most important future technologies. The project also focuses on how Norway's funding of R&D in materials technology can attain traditional materials. During the project, several future analyses will be carried out, describing the major challenges in the field of materials technology towards 2020. These analyses will form a knowledge base for the Research Council's strategic work with materials technology and nanotechnology.

NANOMAT began in 2002, but the firm n-TEC had already been formed the year before to develop a process for the mass production of carbon nanotubes on a carbon-carbon arc process. Today a small scale commercial production has been established, and research carried on in near collaboration with the IFE (Institute for Energy Technology), situated at Lillestrøm outside Oslo, and this nuclear facility is already well known for its hydrogen storage systems used in alternative fuel systems for motor vehicles. The IFE nano-laboratory houses the region's first production reactor for nanomaterial, and the research deals with the unique physical, chemical and electrical properties of carbon nanotubes of importance for future industrial applications of nanotubes.

FUNMAT (Functional Materials and Nanotechnology) is another high-level nano research project that coordinates cross-disciplinary investigation at the University of Oslo, NTNU (Norwegian University of Science and Technology), IFE (Institute for Energy Technology), and the industrial and technical research foundation SINTEF.

The modest commercial production of carbon nanotubes at n-TEC/IFE is the only commercial engineered nanoparticle production facility in Norway for the time being. They are exclusively multi-wall nanotubes generated by the arc method which gives the highest quality material. They have diameters ranging ca. 2 - 50 nm and typical length 2 μm (Figure 10 left). N-TEC also collaborates with SINTEF in Trondheim Norway for production of Conic Carbon nanoparticles with various shapes, through a plasma process, developed in collaboration with SINTEF. These structures are delivered with maximum base diameter: ca. 1-2 μm and wall thickness: ca. 20 – 50 nm (Figure 10 right).²

• ² <http://www.n-tec.no/>

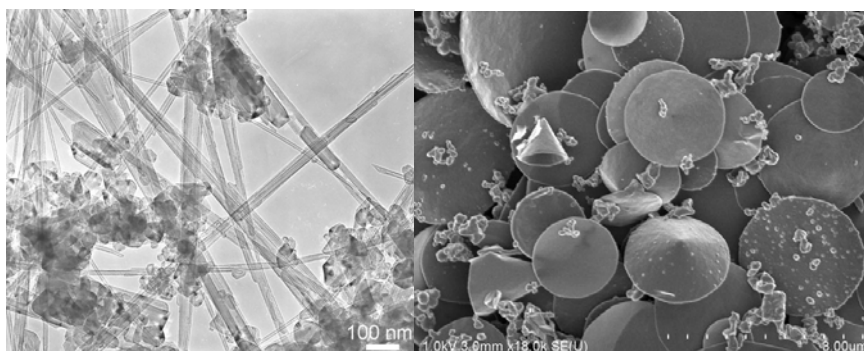


Figure 10. TEM picture of MWCNT (left) and SEM pictures of carbon cones and carbon discs (right). From <http://www.n-tec.no>

For research and development Nanotubes are also produced at NTNU by a catalytic process basically from CO or CH₄. At some industrial research sites in Norway carbon nanofibres are also produced from gas

2.5.2 Ultrafine materials

SiO₂

Annually the recovery of this formerly waste fume in the Norwegian silicon and ferrosilicon industry is around 100 000 tons³. It is now sold as Elkem Microsilica ® as an important reinforcement component mixed in cement. Microsilica is a pozzolana – a term derived from the ancient Italian town of Pozzuli, where volcanic ash was mixed with burnt lime to make cement. This means that it will react with the calcium hydroxide given off by the cement hydration and form more of the calcium silicate hydrate crystal structure that binds concrete together. Because the microsilica is typically over 90% SiO₂, the reactive component, it is a very powerful pozzolana. The large surface area and the high content of amorphous silicon dioxide gives Elkem Microsilica superior pozzolanic properties.

Microsilica has been called the industry's most important new product in the 1990's, and has given civil engineers another tool in the design and construction of structures for the future, due to the durable infrastructure of this cement. Bridge construction (e.g. the Öresund Bridge), marine structures, parking structures, water supply and sewage facilities all benefit from the use of microsilica. Likewise, the addition of microsilica gives benefits in fresh concrete properties, improving the rheology for better pumping and stability of the concrete mix. Special concretes like high strength, self-compacting, light weight, shotcrete and low permeability concretes are better made with microsilica⁴.

• ³ Information obtained from Elkem Materials Sale Department, 2006

• ⁴ Source: <http://www.materials.elkem.com>

Elkem Microsilica® is also a key ingredient in advanced low, ultra-low and cement-free castables. It is highly reactive during sintering, which leads to improved ceramic bonding at reduced firing temperatures, and is also employed in mortars, gunning mixes and other unshaped material. Typical areas of application are within the steel, foundry, cement, glass and ceramic industry. Other areas for use of Elkem Microsilica® are as a grout cement additive and for production of special oil well-drilling reagents, and as an additive in the plastic and rubber industry (PP/PE).

Mn_3O_4

Fumes during production of Mn-alloys are also recovered to prevent environmental pollution. This fume contains ultrafine particles (median size approx 200 nm) and bulk composition similar to Mn_3O_4 . In two Norwegian Mn-alloy smelters approx. 10 000 tons of this fume is recovered and used as an additive to feeds and oil well reagents and as a pigment in brick and ceramic production.

Other

At NTNU in Trondheim the Institute of Material Science has installed a spray pyrolysis production unit for nanocrystalline ceramic powders (Figure 11). The production capacity is 1-10 kg powder per day. Of special interest are the patented LaNbO_4 , Li_2ZrO_3 and La_2NiO_4 powders (Tor Grande, NTNU).



Figure 11. Spray pyrolysis production unit for nanocrystalline ceramic powders at Trondheim the Institute of Material Science.

2.6 Sweden

2.6.1 Introduction

A report from the Swedish Governmental Agency for Innovation Systems states that Sweden has relatively few nanotechnology enterprises in an international perspective (Perez and Sandgren, 2007). In Sweden 85 enterprises applying nanotechnology to some degree have been identified. Of these 34 may be classified as genuine nanotechnology enterprises with their operation based on nanotechnology. The remaining 51 are enterprises applying nanotechnology to a varying extent to support their operations.

None of the enterprises produce engineered free nanoparticles even if nanoparticles may be present in closed production processes. For instance at the Nanotec Forum, Expo and conference in Stockholm in October 2006 none of the 28 exhibitors or 26 presentations dealt with free engineered nanoparticles (including carbon nanotubes).

The Royal Swedish Academy of Engineering Sciences (IVA, 2006) states that Sweden, unlike most developed countries, lacks a national program; in an international perspective Swedish research in nanoscience is ranked relatively high, but the number of nanopatents is relatively low and Swedish research is not commercialized to any considerable degree; and that a proper public debate of the risks of nanotechnology is missing.

In general Sweden has a considerable activity in nanotechnology mostly represented in surface coatings (industry and research), nano-scaled external and internal structures for electronics (mainly research), biotechnology (research and industry). There is no production of engineered nanoparticles and it may be speculated that most nanoparticles to be applied in production in the near future will be imported in preparations and other matrices or semi-manufactured products.

2.6.2 Carbon nanotubes

SAAB AB has extensive experience of carbon fibre reinforced epoxy structural composites. SAAB is now performing research on and development of the application of carbon nanotubes in composites. Of interest, besides increasing the structural strength, is the possibility to design other properties, such as electrical or thermal properties. Carbon nanotubes may be dispersed in the epoxy or integrated into carbon fibre bundles.

The aim of SAAB is to develop applications and to define criteria for composite resins incorporating the carbon nanotubes. The resins with integral carbon nanotubes will be bought from external suppliers and thus no handling of free carbon nanotubes is planned for the production at SAAB. SAAB is concerned about potential risks from the use of raw materials and composites with incorporated nanotubes in production

processes and desires more information on occupational health risks and their control.

Nordic Sport is one of the worlds leading producers in advanced sport equipment. They have specialised in equipment in composite materials. For producing elite javelins they use imported resin impregnated carbon fibre. The material has been stated to be "nanoscale carbon fibre reinforced". However, as far as Nordic Sport knows there are no carbon nanotubes in the material. The producer of the material is Garbolino, France, and no mentioning of carbon nanotubes has been found on their site (www.garbolino.fr). The javelins are formed and cured by Nordic Sport and after finishing a steel tip is mounted and a surface lining is applied.

2.6.3 Photo catalytic concrete

A European Community Eureka-project "Nanocrete" has the aim to develop functional concrete with photo catalytic properties, antibacterial surfaces and the capability to react with and remove nitrogen oxides from the air. Within the project, photo catalytic reactions in cement-based materials containing photoactive titanium dioxide will be studied to see how they can be utilized to obtain clean and functional concrete surfaces. Further technology for production of functional concrete surfaces will be developed.

The project is performed in collaboration between Finnish Kemira, producer of TiO₂ nanoparticles, Swedish construction companies and Swedish research institutes. The Swedish participants are Cementa AB, Skanska AB, Betongindustri AB, Abetong, the Cement and Concrete Research Institute, and the Institute for Surface Chemistry.

2.6.4 Colours, inks and coatings

Svenska Färgfabrikanters Branschförening (The Swedish Paint and Printing Ink Makers Association) believes it is unusual with nanoparticles in products of their members. They are not aware of any nanoparticle production in Sweden.

Heidelberg Maxit Airfresh is an indoor plaster sold in Sweden. It is stated to have a photo catalytic action. It is delivered as powder in paper bags. It "is a gypsum-based plaster that incorporates nano particles of a specially-modified Titanium Dioxide (TiO₂) catalyst"⁵.

2.6.5 Cosmetics

According to Kemisk-tekniska Leverantörförbundet (The Swedish Cosmetic, Toiletry & Detergent Association) there are few developed applications of nanoparticles in their trade marketed in Sweden. Internation-

• ⁵ www.maxitlwa.co.uk/media/43/pdfs/airfresh/airfresh%5Freport.pdf

ally there are a large number of new patents comprising nanoparticles, so possibly there may be an increase of cosmetic nanoproducts marketed. No nanoparticles for cosmetics etc. are produced in Sweden.

2.6.6 Nanoscale surface coating

Impact Coatings develops processes, production technology and applications for thin film coating as well as providing production for customers. The Swedish FunMat program at Linköping University⁶ aims at developing processes for ceramic high-temperature and chemically stable thin film materials.

Pilkington Float Glas AB is a supplier of self cleaning glass panes. The active layer has erroneously been considered to be based on nano TiO₂ particles. In fact a TiO₂ layer is deposited by a high-temperature gas-phase process which gives a nanoscale structure. There is no production in Sweden.

2.6.7 Surface protection consumer products

Some consumer products for surface protection or treatment of among others car windshields, car and boat bodies, ceramics and textiles are marketed as “nano”. Such products are sold but not known to be produced in Sweden.

It is not clear to what extent these products contain nanoparticles or form nanostructures and to what extent it is a marketing phenomena. The year 2005 a fair number of consumer products in Sweden were promoted as “nano” and two years later considerably fewer.

2.6.8 Textiles

There is likely to be some import of nanostructured or nanoparticle treated textiles.

2.6.9 Metal powders

Höganäs AB and Carpenter Powder Products AB manufacture metal and metal oxide powders by gas atomization. Typical size range is from some 10 µm to a few 100 µm. The term “fine powders” seems to be used for powders of particle sizes less than about 50 µm. However, considerable nanoparticle generation emanates from gas atomization processes posing a risk of unintentional nanoparticle exposure. Höganäs AB states that they are not at present heading for nanoparticle production, since with present applications of their powders smaller particles will rather cause

• ⁶ www.liu.se/funmat

handling problems than better performance. However, they are employing and developing powder particle surface modifications on a nanoscale.

2.6.10 Steel

Sandvik AB provides a steel Nanoflex® Alloy. It has been stated or interpreted to contain nanoparticles. The fact is that the steel has an internal nanoscale grain structure due to choice of alloy and processing.

Sandvik Hard Materials AB is reported to have no current plans to apply nanoparticles in production of ceramics coatings for carbide cutting tools.

2.6.11 Colloid silica

EKA Chemical AB produces colloidal silica (amorphous SiO₂). The process is performed in solutions and the products are colloidal silica sols with particle sizes from 5 nm to 100 nm and with around 30 % particles by weight. The colloid silica comes in a variety of grades, covering both mono-dispersed and poly-dispersed types and can be delivered with varying pH, concentration or charge, as required.

There have been thoughts on developing also dry products but these thoughts have for one thing been hampered by the lack of data on potential nanoparticle risks. EKA desires more information on potential occupational health risks.

2.6.12 Perfluorooctanesulfonate (PFOS)

PFOS compounds have been used for decades and have had a variety of applications from industrial processes to components in consumer products. The main reason for using them is their surface active properties, i.e., hydrophobicity, low friction and low surface adhesion. These are properties at the nanoscale of the final product although the compounds are liquid. PFOS is not produced in Sweden.

PFOS compounds are used as pure compounds or as structures in derivatives and polymer products and can be found in e. g.: fire extinguishing products, cleaning agents, impregnation agents for textile, paper and leather, and additives to paint and lacquers. Environmental risk concerns have lead to a reduction during recent years of the use of PFOS which still however may be found in older products. Today the use is mainly in: fumigants for electrolytic chromium-plating, the semiconductor industry, and hydraulic oils for aviation industry.

2.6.13 Fluoropolymer ski waxes

Ski waxes are often based on polymers of fluorocarbons. Many of these waxes are powders with particles with nanoscale surface structures. There is no commercial production of this type of ski waxes in Sweden.

3. Physical characterization

3.1 Introduction

For full notification of a new substance which may be marketed in a form which gives rise to the danger of exposure by the inhalatory route Dir 67/548/EEC, Annex VII A establishes that a test should be conducted to determine the particle size distribution of the substance as it will be marketed. Accordingly, the notification dossier should include a particle distribution measurement. Annex V of Dir 67/548/EEC does not yet sufficiently cover these testing requirements. Accordingly new or revised methods need to be continuously developed. At present, testing methods are currently under development or revision. This includes the Draft Guidance Document on the Determination of Particle Size Distribution, Fibre Length and Diameter Distribution of Chemical Substances⁷. It includes e.g. use of SEM/TEM for determination of particle size distribution of the material as it is.

Also the determination of the ability of the material to generate airborne dust (dustiness) during handling is essential data for use in an appropriate risk assessment both for new and existing substances. The draft guidance document also includes a dustiness test that is based on the rotating drum test principle, see also section 3.2).

OECD has currently established several working parties for reaching agreement on definitions as well as recommended measures for engineered nanoparticle characterization. The working parties include the following steering groups:

- SG1 - Development of an OECD database on EHS research
- SG2 - EHS Research strategies on Manufactured Nanomaterials
- SG3 - Safety Testing of a Representative Set of Manufactured Nanomaterials
- SG4 - Manufactured Nanomaterials and Test Guidelines
- SG5 - Co-operation on Voluntary Schemes and Regulatory Programmes
- SG6 - Co-operation on Risk Assessment.

At this point, the working document from SG3 proposes the following input parameters for engineered nanoparticle characterization:

• ⁷ <http://ecb.jrc.it/documents/Testing-Methods/GDoc-Granulometry-draft-web.pdf>

Characterization (primary end-points)	Particle density and dispersability
Technical name	Persistence
Commercial name	Ready biodegradability
Chemical composition	Agglomeration
Molecular structure	Persistence of nano-property
Crystal structure	Base Set of Safety Hazard Data
Physical form at room temperature	Flammability
Pressure at room temperature	Explosivity
Surface area	Incompatibility
Particle size distribution and average diameter	Reactivity
Solubility in water and biologically active fluids	Corrosivity
Bulk density	Additional Safety Hazard Data
Agglomeration state	Stability
Porosity	Decomposition
Surface charge sites	Polymerization
	Photoactivity
	Thermal/light stability

As the OECD parameters originate from a working document, some items may possibly be merged and others added.

The analyses proposed by OECD are presently limited to a small number of laboratories. For a first step physical characterization, the project group recommends to follow Table 3.

Table 3. Physical characterization of nanomaterials

Parameter	Bulk material	Aerosol (dispersed state)
Particle size	TEM/FEGSEM	SMPS, TEM
Particle morphology	TEM/FEGSEM	TEM/FEGSEM
Agglomeration state	Dynamic light scattering or tracking analysis	SMPS, TEM
Specific surface area	BET	Surface concentration based on diffusion charging
Crystallinity	XRD	TEM/SAED
Elemental composition	TEM/EDX	TEM/EDX

Nanoaerosols are dynamic entities. Once formed and released as an aerosol, nanoparticles may undergo significant changes in size distribution and concentration, surface chemistry, and surface charge depending on the local environment and primary properties (SCENIHR, 2007). During aerosol sampling and subsequent sample preparation further changes may be introduced. According to the experience by members of the group, some types of nanoparticle suspensions agglomerate during mild sonication and strong sonication is used e.g. in some industrial process to break agglomerates. Dust generated when handling a specific ultrafine TiO₂ having a primary particle size of about 20 nm generated agglomerates of

the order 300nm. When suspended in a liquid simulating lung fluids they de-agglomerated, but not down to the primary particles (Maynard, 2002).

Meticulous registration of test conditions and of sampling and analytical methods thus is indispensable. The project group noted that state of agglomeration and how to quantify this was a key problem.

3.2 Characterization of pigment grade and ultrafine TiO₂ and fumed silica

The three powders

- Kemira AFDC (an uncoated anatase titanium dioxide pigment)
- Kemira UV-TITAN M111 (an alumina treated ultrafine rutile titanium dioxide)
- Elkem Microsilica Grade 920 (dry silica fume)

were characterized. The methods used for characterization were:

- X-ray diffractometry for phase analysis
- BET-analysis for specific surface area determination
- Electron microscopy for imaging and elemental analysis. Samples were prepared by dispersing the powder into distilled water and then placing a droplet of the powder dispersion onto a holey-carbon Cu-grid.

The results are presented in Table 4 and Figure 12-14.

Table 4. Physical characteristics of pigment grade and ultrafine TiO₂ and fumed silica.

Material			
Parameter	Kemira AFDC (an uncoated titanium dioxide pigment)	Kemira UV-TITAN M111 (an alumina treated ultrafine rutile titanium dioxide)	Elkem Microsilica 920
Particle size	Crystallite size ~170 nm ^a	Crystallite size ~14 nm ^a	~150 nm ^a 80 w% <5 µm
Particle morphology	Round-shaped forming agglomerates of several particles	Needle-shaped, forming agglomerates of size 10 and more	Spherical, forming agglomerates of several particles
Dispersion state	NA	NA	NA
Specific surface area	5.5 m ² g ⁻¹ (~10 m ² g ^{-1 a})	112 m ² g ⁻¹ (ca. 100 m ² g ^{-1 a})	12 m ² g ⁻¹ (> 15 m ² g ^{-1 a})
Crystallinity	Anatase	Rutile	Amorphous
Elemental composition	Ti, O	Ti, 3%w/w Al	Si, O, traces of Ca, Na

^aFrom manufacturer. NA: not available.

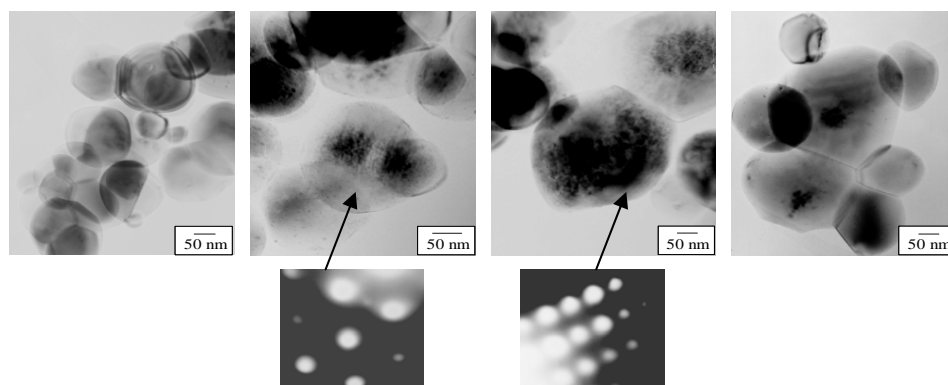


Figure 12 Kemira AFDC. Electron diffraction from the particles showing the crystallinity of particles.

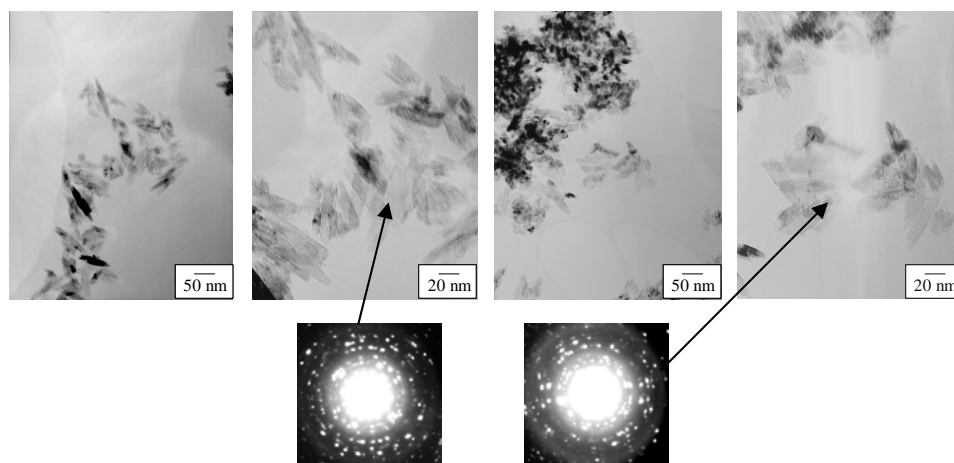


Figure 13 Kemira UV-TITAN M111. Electron diffraction from the powder shows the crystallinity of nanoparticles.

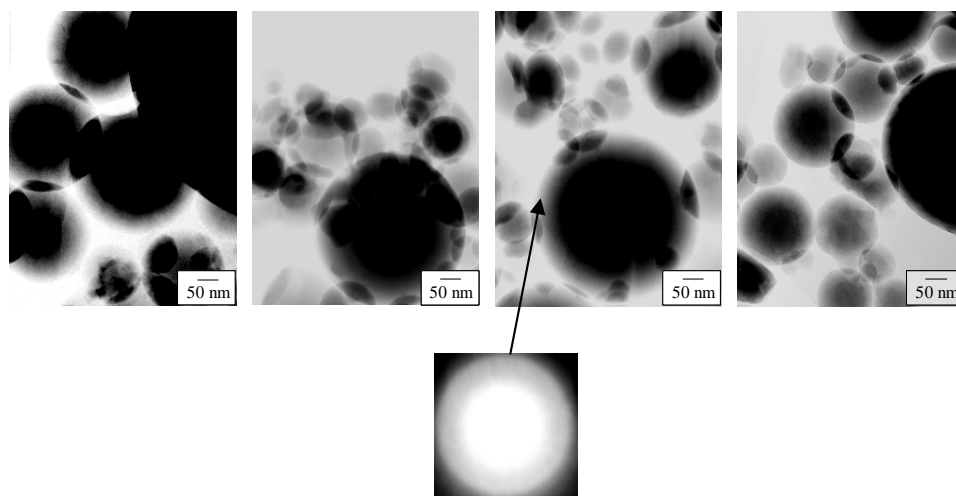


Figure 14. TEM of Elkem micro silica.

3.3 Dustiness of powdered, granular or pelletized nano-materials

Handling of nanomaterials generates dust. The amount and size distribution of generated particles will depend on the handling scenario and on the material properties. Many dustiness tests have been developed using many different approaches for simulating real handling scenarios (Gill *et al.*, 2006). For testing e.g. pigments the Heubach Dust meter (DIN 55992-1 part 1, 1997) has been widely used. It is based on a small rotating drum.

Recently, the European standard EN 15051 (CEN, 2006) on dustiness testing in relation to workplace exposure (Liden, 2006) has been published. It defines a dustiness index as the mass ratio of generated dust in mg to the mass of test sample in kg. The dustiness index may be obtained by two methods: one based on a rotating drum and another based on a continuous single drop principle. Users of this standard should choose the one of the two methods that is most appropriate for the material and handling process they wish to simulate. The EN 15051 also defines a classification according to the dustiness index as obtained with the two methods, and for both the respirable, thoracic (rotating drum only), and inhalable size fractions of the generated dust, respectively. The two testing principles lead to different classification and different ranking within each class (CEN 2006). This problem needs to be resolved before a dustiness test can be implemented in legislation.

3.3.1 Existing dustiness tests

Simulation of pigment handling (Aerosil, nominal particle size 7 nm) as performed in the dye industry has been reported by Bohgard *et al.* (1994). They found a source strength of 4×10^5 particles s^{-1} for particles in the size range 20-1000 nm with a mode around 120 nm and another mode at about 1.3 μm in the size range 1-10 μm with a source strength 5×10^5 particles s^{-1} .

Aerosil 200 (a hydrophilic fumed silica having a specific surface area of 200 m^2/g BET or median diameter 12 nm) has been tested using the Heubach Dustmeter as standardized by DIN 55992. The measured dust value corresponded to a dustiness of 1% (Hamelmann and Schmidt, 2004). It was also found that a specific single drop method ranked the dustiness of limestone, aluminium oxide and fumed silica differently than the Heubach Dustmeter.

Maynard (2002) and Maynard *et al.* (2004) developed a dustiness test for nanosized powders based on fluidization. Fluidization was obtained by placing milligram amounts of material with or without 70 μm bronze beads in a centrifuge tube agitated by a vortex shaker. By this technique the dustiness as a function of the force applied to the powder can be stud-

ied. (Maynard, 2002) tested an ultrafine TiO_2 powder (Degussa Aeroxide P 25, $50 \pm 15 \text{ m}^2/\text{g}$) using the fluidization principle (material and $70 \text{ }\mu\text{m}$ bronze beads in a centrifuge tube placed on a vortex mixer). The particles were quantified using an SMPS and APS. A bimodal size distribution was found with number modes 330nm and $1.8 \text{ }\mu\text{m}$, the latter mode being about 0.4 times the first.

Maynard *et al.* (2004) also tested SWCNT using a fluidization principle by placing a small quantity (40 mg material and $70\text{ }\mu\text{m}$ bronze beads or 15 mg without beads) in a centrifuge tube agitated by a vortex shaker. During actual handling of carbon nanotubes, low concentrations of particles were generated. The authors concluded that nanotubes do not readily become airborne during handling.

3.3.2 Development of dustiness test for small amounts of powder and results

In connection with the present project, a new dustiness test was developed. The design and the results of dustiness tests are given in Schneider *et al.* (submitted). The following is a brief summary. The purpose of developing the new dustiness test was to obtain a method that used minimal amount of material and that in a simple manner could bridge the two test principles given in EN 15051. The test apparatus is based on a down-scaled version of the EN 15051 rotating drum, while maintaining important test parameters (Figure 15). The test begins with a single drop challenge and then continues with a 60 sec rotation of the drum performed on the same sample. Since the time dependent dust emission rate is another important aspect of powder dustiness the instantaneous dust concentration was monitored using the TSI Fast Mobility Particle Sizer and the TSI Aerodynamic Particle Sizer, both with one-second time resolution. The measurement range was $0.52\text{--}19.8 \text{ }\mu\text{m}$ for the APS and $6.04 \text{ to } 523 \text{ nm}$ for the FMPS. The total mass of particles generated for the total duration of the test was determined by collecting the particles on a filter and determining the weight gain of the filter. This test uses 6g of material per run, as compared to the 200 g or more in the EN 15051 methods. This makes the apparatus suitable for testing costly materials. Its small size allows easy placement in a fume cupboard and thus potentially very toxic materials can be tested.

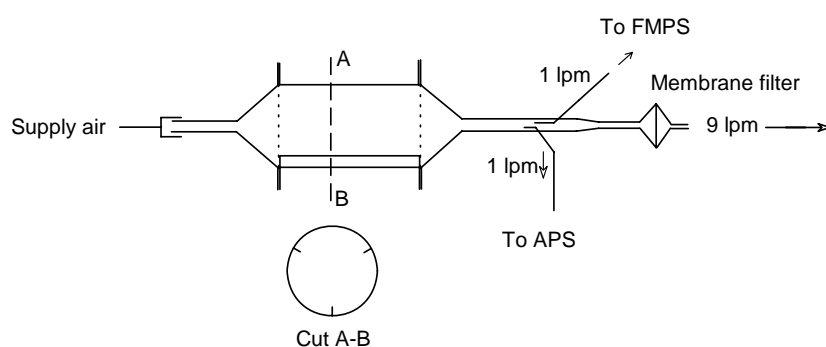


Figure 15. Rotating drum dustiness tester

Tests were completed on the materials shown in Table 5. Characteristics of the pigment grade and ultrafine TiO_2 and fumed silica can also be found in section 3.1. Micrographs of the yttrium stabilized zirconia granules used in the dustiness test are shown in Figure 16. Notice that the material was granulated, with granule diameter about $50\mu\text{m}$.

Table 5. Specifications of the test materials.

Material	XRD crystallite size, nm	Specific surface area ^a , m^2g^{-1}	Bulk density major component, g cm^{-3}
TiO_2 ultrafine, rutile	18.6 (14 ^a)	100	
Fumed silica	Amorphous	15–30	2.2 ^a
Bentonite (montmorillonite)	8.2 ^{c,d}	NA	2–3 ^b
Yttrium stabilized zirconia	27	15.4	6.05 ^a
Goethite	38	18–21	4.3 ^b
Corundum, aloxite F1200	92	NA	3.96 ^b
Corundum, aloxite F800	127	NA	3.96 ^b
Talc	147 ^d	NA	2.58–2.83 ^b
TiO_2 pigment grade, anatase	170 ^a	10	4.23–5.50 ^b

NA: Not available. ^a Data from manufacturer, ^b Deer *et al.* (1985), ^c Mean for samples from Jonas and Oliver (1967), ^d Height of tabular-shaped crystallites size along the crystallographic (001).

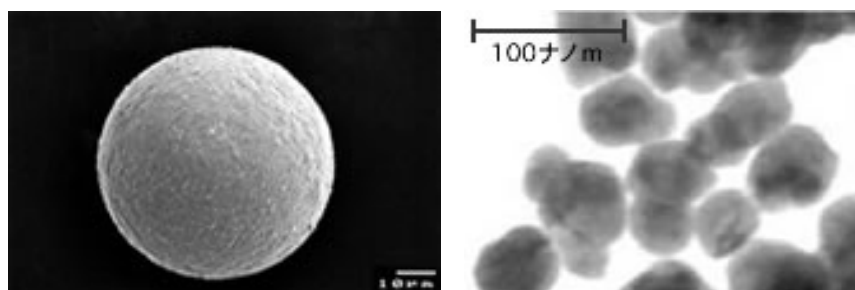


Figure 16 Yttrium stabilized zirconia. SEM picture (left) shows a granule (length of bar $10\mu\text{m}$). TEM picture (right) shows the aggregated primary particles (length of bar 100nm). From http://www.tosoh.com/Products/basic_grades.htm

The size distributions of the generated aerosol had two size modes above 0.9 μm and all materials except TiO_2 pigment grade and aloxite F1200, generated a size mode in the range from ~ 100 to ~ 220 nm. Examples are shown in Figure 17. This figure should be contrasted to Figure 18 showing the corresponding volume-weighted size distribution. The large difference in fraction of sub-micron particle numbers and sub-micron particle volume (or mass) should be noticed. Notice also the log-scale.

TiO_2 pigment grade had the lowest dustiness and TiO_2 ultrafine the highest dustiness as measured by particle number for both the single drop and rotation test and as measured by mass for both tests combined. The difference was a factor of ~ 300 . A similar large difference in exposure potential can be expected. This would imply that preventive measures would have to be much stricter if the pigment grade TiO_2 were to be replaced by the ultrafine version. Since aggregates of ultrafine TiO_2 can brake up in the lung fluid and assuming particle number matters, the potential risk would even be larger. An increasing trend in dustiness was found for decreasing crystallite size.

A ratio, R , defined as

$$R = \frac{D_{\text{sd}}}{D_{\text{sd}} + D_{\text{rot}}}$$

was determined, where D_{sd} is dustiness index determined from the single drop, and D_{rot} is dustiness index determined from rotation test. It was found that R varied within a factor of 40 for the tested materials. When analysing the time dependent particle generation rate during the test, it was found that there were three types of time profiles: i) a brief initial burst (talc, both grades of corundum), ii) a decaying rate during rotation period (fumed silica, TiO_2 ultrafine and pigment grade, bentonite), iii) a constant rate (Y-zirconia, goethite). As could be expected, materials with a burst profile had a large R , and those with a constant profile had a small R . Such large differences in particle generation time profiles or equivalently differences between a single drop and a rotation dustiness test has implications when having to choose which of the two dustiness test principles given in EN 15051 are best suited in a given exposure scenario.

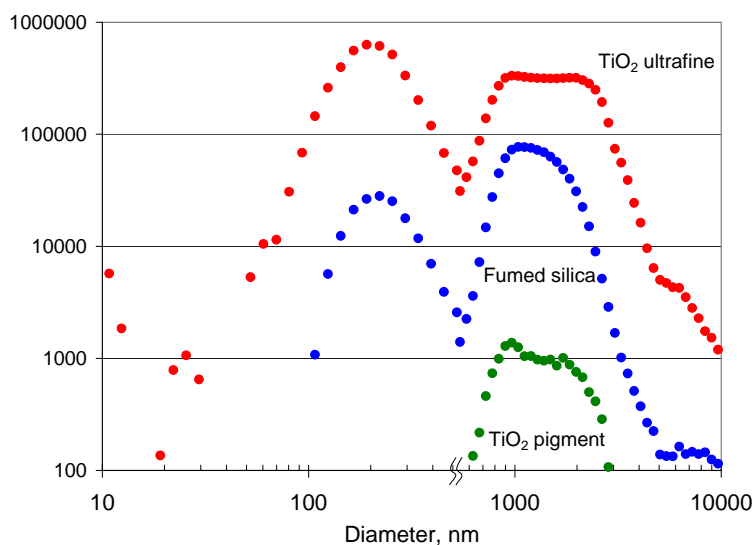


Figure 17 Size distribution by number for ultrafine and pigment grade TiO₂, and fumed silica.

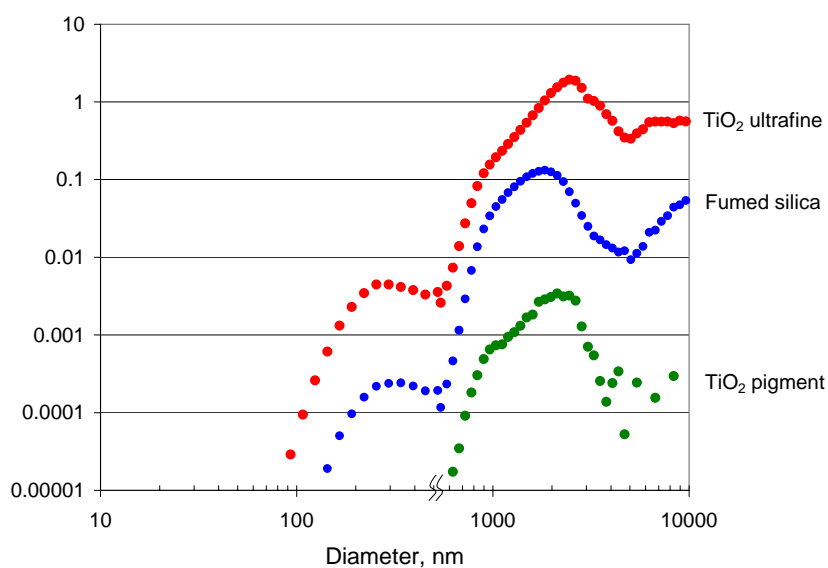


Figure 18. Size distribution by volume of ultrafine and pigment grade TiO₂, and fumed silica

The results indicated also that aerosolization of nanoparticles from a bulk powder results in agglomerates, a fact also noted by Wake *et al.* (2002). Nanoparticles have a natural tendency to aggregate due to the significant attractive forces between particles at nanosize. Processing of nanosized powders by fluidization can be used to modify their properties and large, spherical aggregates are formed when intra-aggregate forces are stronger than inter-aggregate forces (Hakim *et al.*, 2005).

4. Assessment of exposure and control measures

4.1 Introduction

Among the many workplace factors that may increase the potential for exposure to nanoaerosols, NIOSH (2007) has listed the following:

- Generating nanoparticles in the gas phase in non-enclosed systems will increase the chances of aerosol release to the workplace
- Collecting, handling and conditioning nanostructured powders will lead to the possibility of aerosolization
- Working with nanomaterials in liquid media during pouring or mixing operations, or where a high degree of agitation is involved, will lead to an increased likelihood of inhalable and respirable droplets being formed
- Maintenance on equipment and processes used to produce or fabricate nanomaterials will pose a potential exposure risk to workers performing these tasks
- Cleaning of e.g. dust collection systems used to capture nanoparticles.

In addition several down-stream uses and final product utilizations may result in potential exposure such as use of polishing compounds, cutting and grinding/sanding of nanocomposites, and degradation of nanosurfaces.

Accidental releases can occur during nanoparticle generation using high pressure or high energy mechanical forces could occur in case of failure of the sealing of the reactor or the mills. In such situations large amounts of nanoparticles could be released in short bursts. For laser processes, breaking of reactor laser windows is a possible source (Luther 2004).

Collection of nanoparticles in liquid suspensions reduces dust emission (Luther, 2004). Master batches are increasingly used by downstream users thereby concentrating the dust problems at few up-stream suppliers. Silica fumes are mostly supplied to down-stream users as slurries.

There is a wide gap in information on the risks to specify which levels of control are required and thus to provide guidance on choice of proper control measures. However, several approaches developed for conventional materials provide a conceptual framework for describing and analysing exposure scenarios and specific control approaches for nanomaterials. These will be described in the following.

4.2 The COSHH Essentials concept

A useful concept for defining appropriate control levels in relation to conventional powders and materials is control banding. *COSHH Essentials*⁸ is such a control banding tool. It is intended for helping small and medium-sized enterprises doing risk assessments for chemicals and mixtures of chemicals. COSHH stands for *Control of Substances Hazardous to Health*. This tool requires four pieces of information, which in the case of particles are:

1. The type of task (e.g. mixing, sack filling, manually cleaning surfaces)
2. The hazard group from the material safety data sheet, or SDS, part 15 (one of groups A to E, with E the most hazardous and group S representing substances which can cause harm as a result of skin contact). These are based on the risk phrases for the chemical, which are given in Section 15 of the SDS obtained from the chemical manufacturer or supplier
3. The dustiness of the material or product (low, medium or high, based on simple descriptors)⁹.
4. The amount used in the task (small quantities = grams; medium quantities = kilograms; large quantities = tons)

The system then

1. Identifies the control band (control approach). There are four control approaches:
 - a) general ventilation
 - b) engineering control
 - c) containment
 - d) users are directed to seek specialist advice for the most hazardous chemicals and tasks
2. Produces advice on controlling risk from the chemical used in the specified task
3. Provides written guidance and documentation as a result of the assessment.

Similar schemes are used in the practical guidance given by the The German Federal Institute for Occupational Safety and Health (BAuA, 2006). The Stoffenmanager Dutch (van der Schaaf *et al.*, 2006) represents a further development, see section 4.3.

⁸ <http://www.coshh-essentials.org.uk>

⁹ Mark (2004) has proposed to replace the descriptive terms in COSHH Essentials by a the dustiness index of the material

(Maynard, 2007) has proposed to use an analogous for nanomaterials. According to Maynard (2007), it should in principle be possible to assign an

- Impact index based on hazard (as based on material composition) and modifications due to the nanostructure
- Exposure index representing the amount of material used and the dustiness.

See also Figure 19

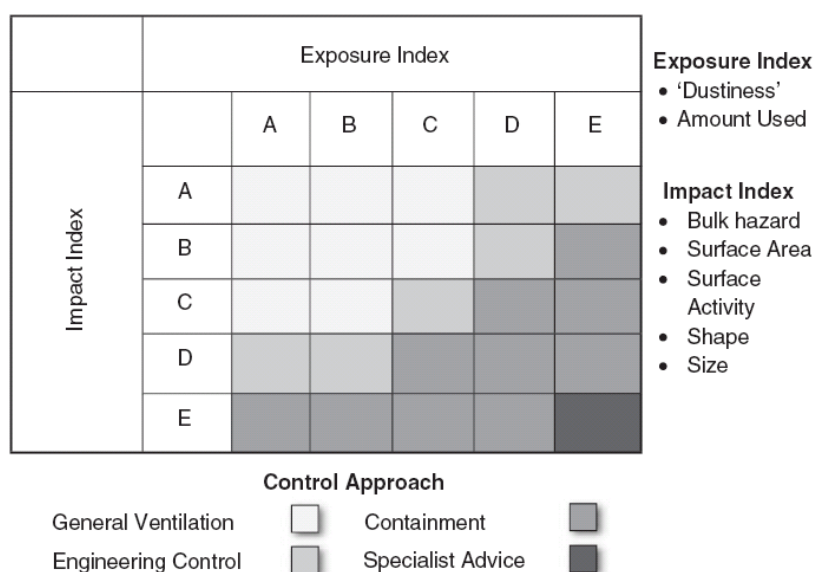


Figure 19. Proposed control banding for nanomaterials (Maynard, 2007).

4.3 REACH scenarios

There is yet no official Technical Guidance Document on how to define exposure scenarios for REACH. The following outline has been suggested in the Technical Guidance Document on Risk Assessment (2003) and by Christensen *et al.* (2003):

An exposure scenario (for manufacturers or identified downstream users) as annexed to a Safety Data Sheet sets out how the substance can be used in a way that risks are adequately controlled by describing:

- Conditions for use
 - Process description, incl. quantity used
 - Operational conditions, incl. frequency of duration of specified operations
 - Risk management measures
 - Process and emission control
 - Personal protective equipment

- Good hygiene
 - Etc.
- Other relevant information
- Exposure level associated with the described scenario
- Exposure scenario shall cover
 - Manufacture and all identified uses, incl. maintenance related exposures
 - All life cycle stages resulting from manufacture and identified uses

For each defined scenario the most relevant moments of exposure should be described. Figure 20 illustrates a hypothetical exposure scenario for the downstream use of a substance in paint.

Exposure scenario: paint for indoor use	
Composition	Concentration of substance X < 10% No organic solvents
Use characteristics	Spray painting
Duration and frequency	8 hours per day, 200 days per year
Cleaning	Equipment can be cleaned with hot water and detergent
Risk management measures	Wear mask and gloves during use Provide ventilation in rooms, with a replacement rate of 1 per hour Containers and other waste must be treated as hazardous waste—that is, delivered to a collection system Liquid waste, including cleaning water, may be disposed of via the sewage system, if connected to a sewage treatment plant (unless other paint constituents require differently); otherwise it must be treated as hazardous waste

Figure 20. Hypothetical exposure scenario, from Christensen *et al.* (2003).

4.4 Modelling

The European REACH Implementation Project RIP 3.2 initiated by the Commission has proposed a tiered approach in which the first tier should provide a conservative (i.e. protective) system that can discriminate between substances in scenarios of some concern and those which are not (RIP 3.2, 2005). The Stoffenmanager (van der Schaaf *et al.*, 2006) may be a good candidate for this first tier because a preliminary validation exercise has shown that for dusts, the Stoffenmanager could explain 65% of the variability of measured dust concentrations ranging over six orders of magnitude (Tielemans, 2007). It is based on the deterministic model

developed by Schneider *et al.* (1991), Cherrie *et al.* (1996), Cherrie (1999), Semple *et al.* (2001), and Cherrie *et al.* (2004). This original model comprises an air contaminant source term which is dependent on intrinsic properties of the contaminant (ε_i) (e.g. dustiness), the way the contaminant is handled (h) and finally, the effectiveness of any local control (η_{lv}). The parameters are combined to provide the active emission of the source (ε_a). Three further parameters are incorporated in the basic model. These are the passive or fugitive emission (ε_p), the fractional time the source is active (t_a) and the efficiency of any respiratory protection (η_{ppe}). So for a single source close to a worker, the exposure level, C , would be

$$C = (\varepsilon_i \times h \times (1 - \eta_{lv}) \times t_a + \varepsilon_p) \times (1 - \eta_{ppe})$$

The passive emission term is included as an additive term unrelated to the active source.

The full model distinguishes between contribution from sources close to and far from the worker and the role of general ventilation. There is insufficient nanoparticle specific data to allow such a distinction.

Exposure for each individual task is calculated separately and time weighted to calculate the time-weighted average exposure.

Intrinsic emission is the potential for the substance to become airborne. For the convenience of the assessor using the model, intrinsic emission is generally expressed in relation to a “target value”, often chosen to be the occupational exposure limit (OEL)¹⁰.

Handling represents the methods by which the substance is handled and also the amount of energy being put into the substance while handling.

If there is no local exhaust this parameter should be set to 1. If local exhaust is installed or other controls are in use this parameter may be set to 0.3. If the local ventilation is very well designed and maintained or there are other efficient controls, this may be set to 0.1.

Passive emission is the amount of substance released from fugitive emissions or passive sources e.g. dust from conveyors. It may also be released from sources not directly associated with the process e.g. resuspension of settled dust. It is therefore affected by the cleanliness of the workplace, with cleaner workplace having a lower passive emission. Passive emission is generally much less than active emission. Although, passive emission relates to intrinsic emission in that a more dusty material is likely to have a higher passive emission than a less dusty one, it also depends on the cleanliness of the workplace.

• ¹⁰ For NP materials such target values are not yet available and will have to be based on future systematic workplace measurements performed using generally recognized sampling and analytical methods.

Use of the model will increase standardisation of exposure data collection and assessment and provide a framework for analyses of exposure data (Tielemans *et al.*, 2007). The model elements should be seen as providing “building blocks” for development of exposure models for specific scenarios.

4.5 Dose

Respirable dust is defined as the fraction of the inhaled dust that penetrates to the alveoli. It does not address what fraction deposits in the alveoli. This was no severe limitation when studying traditional aerosols because the ratio of respirable mass to mass deposited in the alveoli was fairly constant. However, when the focus is on nanosized particles and in particular if particle number or surface area, rather than particle mass is a potential risk measure, this is not so. The alveolar deposition is shown in Figure 21 (Hinds, 1999). It is seen that there are two deposition maxima and it is of relevance for risk assessment, to determine these two size fractions separately. At present this is only possible by determining the size distribution and then to numerically extract this information.

Ingestion of engineered nanoparticles is of concern. Let it be assumed that the particles are chemically stable, that growth due to hygroscopicity can be neglected, and that all particles deposited in head and tracheo-bronchial region are cleared and swallowed. The ratio of particles reaching the gastro-intestinal tract to particles depositing in the alveoli can then be calculated as the ratio of number of particles deposited in the head and tracheo-bronchial region to the number deposited in the alveoli. The result is shown in Figure 21. The tracheo-bronchial and head deposition fractions given by Hinds (1999) were used. It is seen, that below 10 nm and above 10 μm a larger fraction of inhaled particles end up in the gastro-intestinal tract than in the alveoli.

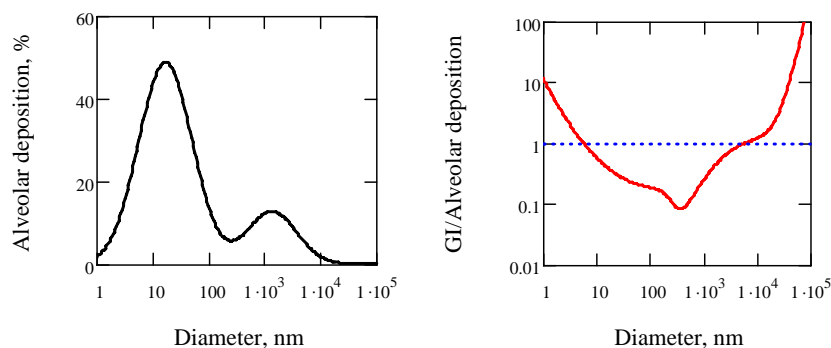


Figure 21 Alveolar deposition fraction, % (left). Ratio of GI deposition to alveolar deposition (right). Airway deposition fractions are from Hinds (1999)

4.6 Control approaches

4.6.1 General

Nanoparticles possess some characteristics that may make them behave somewhat differently from larger particles in workplace environments. However, the differences are not so great as to be of a fundamental importance as seen from an engineering control perspective. A NIOSH report (NIOSH, 2007) states in the executive summary: “For most processes and job tasks, the control of airborne exposure to nanoparticles can most likely be accomplished using a wide range of engineering control techniques similar to those used in reducing exposures to general aerosols”.

The engineering control techniques of nanoparticle exposure can build on the knowledge and experience from current exposure control of aerosols which already today has been applied to aerosols containing ultrafine particles such as e.g. welding fume, carbon black, or viruses. Radical shifts are not needed in general, but rather adaptation and redesign of current technology to deal with certain characteristics of nanoparticles. This applies to techniques for general ventilation, industrial ventilation, local and process ventilation, containments and enclosures, and filtration.

The size and mass of nanoparticles have some related implications for their transport with air flow, their deposition, and their agglomeration as compared with larger particles. They will follow air flow and even turbulent flows well and to a considerably higher degree than μm -sized particles. The particle relaxation time, which is one measure of how rapidly particles follow changes in flow velocities are one to two orders of magnitude smaller for less than 100 nm particles than for 1 μm particles. The practical aspect is that they at large behave in air less like airborne particles and more like heavy molecules, apart from not rebounding from surfaces. Nanoparticles do not exhibit gravitational settling and surface deposition is due to Brownian and turbulent diffusion, static electrical fields, and thermophoresis (transport towards a surface having considerably lower temperature than the surrounding air. This deposition is independent of orientation, see also Figure 25. Coagulation, the process of particles forming agglomerates, leads to a decrease of number concentrations with time, but unchanged mass concentrations. In some circumstances with high number concentrations (of the order of 10^6 cm^{-3} or more) coagulation may lead to significant effects from an industrial hygiene point of view, see also section 4.7.3.

Current practices worldwide in the nanotechnology industry have been surveyed by ICON (2006a). The reported environmental health and safety practices did not significantly depart from conventional safety practices for handling chemicals. Most organizations reported that the biggest im-

pediment to improving their nano-specific environmental health and safety program was lack of information. Thus, a strong demand for industrial and governmental guidance in environmental health and safety practices was identified. It was noted that very few of the guidelines for “best practices” and frameworks for nanomaterial risk management were based on empirical research. Rather, they were based on current knowledge and expert consultation. Figure 22 presents a summary of the designs and engineering controls used (ICON, 2006b). The ICON study only included research laboratory and manufacturing facilities and not e.g. consumer and waste management practices.

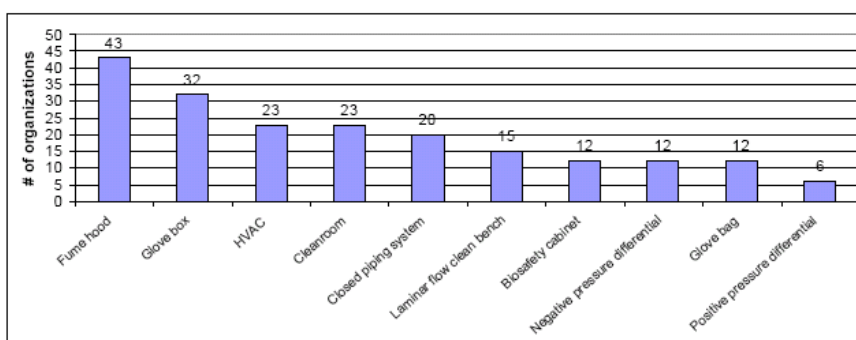


Figure 22. Reported nano-specific facility design and engineering controls. Copied from ICON (2006b).

A very pragmatic approach to risk management adapted from Peters (2005) could be:

- Like for traditional exposure scenarios, most exposures occur due to short peaks originating from point sources. Point sources can be detected by using qualitative exposure assessment based on observation and professional judgement. Potential sources can be identified and their frequency and relative magnitude of release be determined using conventional aerosol photometers. For suspected more toxic particles, an instrument having a suitable sensitivity such as a condensation particles counter should be used. Combining these measurements with visualization of individual execution of work tasks, such as using the PIMEX method (Rosén, 2002) can provide very useful information regarding reduction of emission
- Many commercial receipts are sold in slurry form in order to stabilize the material against aggregation with the added benefit of reducing exposure. Not much is however known of resuspension of nanoparticles from dried spills of slurry from e.g. floors, tools, and clothing.
- Safe practices
 - Laboratory settings. Using a condensation particle counter it should be confirmed that containment is effective.
 - Industrial settings. Existing qualitative exposure assessment methods can provide a sound starting point. This would include

visual inspection supported by suitable aerosol detectors, discussion with operators to assess location and frequency of sources. Also observation of dust build up can provide clues for uncontrolled sources.

The need for increasing the effectiveness of technical control measures can be estimated on a relative scale

- If going from micron to nanosized materials, even if there is no change in toxicity of bulk materials and in order to keep the same exposure a decision tree could be
 - If mass effect – do nothing more
 - If surface area effect – reduce exposure four times every time diameter is halved
 - If number effect – reduce exposures eight times every time diameter is halved
- If nanoparticles are to be added to an existing process and if the existing process is highly enclosed and serviced with engineering controls it may be easy in practice to meet a lower exposure limit
- Risk of explosion¹¹

4.6.2 Filtration of nanoparticles

Filtering performance of conventional porous filtration media of various design have a similar behaviour regardless of filter media characteristics and of air flow rate. For large enough (larger than some μm) particles the penetration is close to 0 % and dictated by deposition due to interception and impaction. With decreasing particle size the penetration increases and displays a maximum at a “most penetrating size” and then, for further decrease in particle size, the penetration will begin to decrease. This decrease is due to deposition by diffusion.

• ¹¹ While important, risk of explosion was not investigated in the present project.

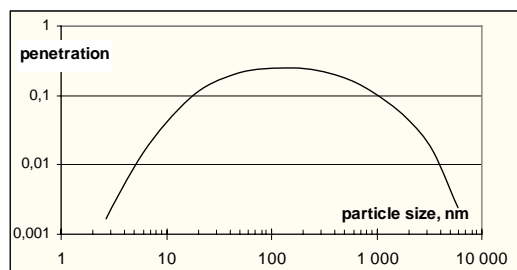


Figure 23. General qualitative penetration behaviour through fibrous filters. The absolute level of maximum penetration may vary with some orders of magnitude depending on filter quality.

This qualitative behaviour (Figure 23) is general for porous filter media and may be well described quantitatively by classical filtration theory. For conventional fibrous filtration media the most penetrating particle size lies around 300 nm, principally depending on air flow rate and fibre diameter. This has resulted in filter classification standards being based on filtration efficiency at this particle size, based on the philosophy that the penetration is lower for all other particle sizes. Recently it has been found that pre-charged filter media, as commonly used in protective filtering face-piece respirators, may have a most penetrating size at 30–70 nm (Balazy *et al.*, 2006). In practice this may lead to an overestimation of the protection with filter masks when the estimate is based on filtration data for 300 nm particles given that particle number exposure is a more significant health risk parameter than particle mass exposure.

Another aspect of interest is that as particles get smaller they behave more and more like molecules and the filtration efficiency will decrease to zero. It is not well known when this behaviour begins and as a consequence there have been speculations on and results indicating that this might begin to occur for nanoparticle diameters of 10–20 nm (Balazy *et al.*, 2004). Later, more elaborated and sophisticated measurements have not shown deviations from classical fibre theory down to 2–3 nm particles (Heim *et al.*, 2005; Kim *et al.*, 2007).

One effect of particle size may be that filter pressure drop will increase faster than for the same mass of larger particles. One theoretical approach predicts a proportionality of $(\text{particle size})^{-2}$ (Endo and Alonso, 2001). It was the experience of the project group that sampling sub-micrometer particles on filters results in higher pressure drops than sampling larger particles. This may support this effect.

Some conclusions can be drawn at large. For nanoparticles the filtration will be better the smaller the particles at least down to some nm particle size. Successful filtration of nanoparticles does not require development of new filtration techniques, albeit new designs may be adapted, and there is a wide range of commercially available filtration media that may be applied in industrial hygiene contexts. Filtration performance may be

dimensioned, controlled, and predicted by existing filtration theories. The filtration performance of pre-charged filter media seems to be overestimated in ratings based on standard test methods.

4.6.2 Personal protective equipment, PPE

According to ICON (2006b), a little over half of the organizations indicated that employees used respiratory protection. Reasons for not using respiratory protection could be that engineering controls were effective, no free nanoparticles were handled, the amount handled was very small, or nanoparticles were only handled in closed processes. Use of recommended clothing is shown in Figure 24.

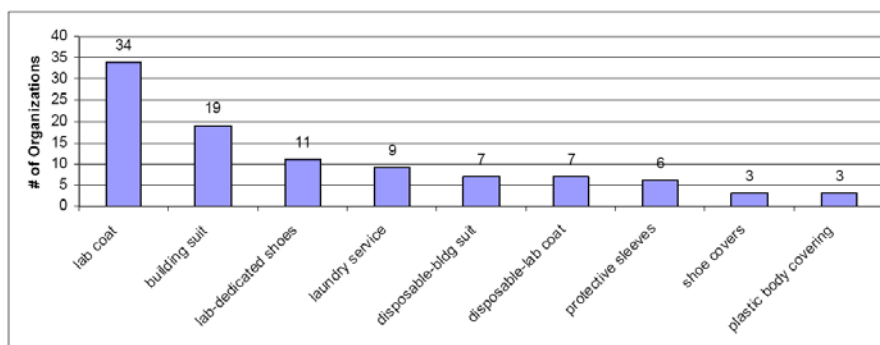


Figure 24. Recommended clothing when working with nanomaterials. From ICON (2006b).

4.7 Some specific points

4.7.1 Visibility

It is well known that dust concentrations cannot be estimated visually. The visibility depends on illumination intensity and geometry, on the background, and on the particle size and concentration. If visible, respirable particles are only seen as a “haze”, not as individual particles. As the particles get smaller, the concentrations need to be higher to be visible, other factors remaining the same. It has been reported¹² that a particle cloud of gram (!) per cubic metre concentrations of alumina nanoparticles is transparent. Exposure assessors therefore cannot assume that even massive leaks will be visible during a walk-thru investigation. Thus suitable particle detectors are indispensable during any exposure assessment exercise.

• ¹² Personal information, Morten Berntsen, Institute of Technology, Oslo, Norway

4.7.2 Surface deposition

Surface deposition will build up secondary sources of dermal, and if agitated, airborne particle exposure. To get an order of magnitude estimate of the importance of this potential exposure route a model calculation has been made. Using the semi-empirical model by Schneider *et al.* (1999) the deposition velocity to a vertical surface the velocities shown in Figure 25, have been calculated. U^* is the friction velocity. U^* scales the air turbulence intensity, the larger, the more turbulent the air. The full drawn lines are for zero electric fields, the dashed lines are for field strength at the surface of 10 kV m^{-1} . An aged aerosol (Boltzmann charge distribution) has been assumed. For particles below about 300 nm deposition velocities will be independent of surface orientation.

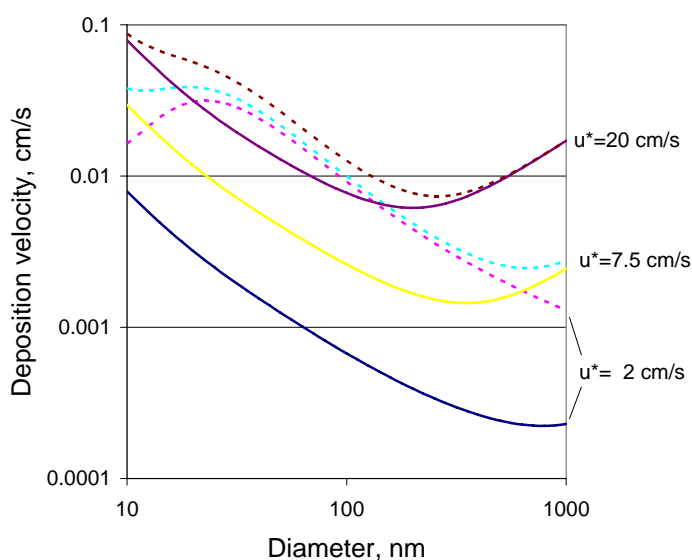


Figure 25. Deposition velocities for different friction velocities u^* and for electrical fields 0 kV m^{-1} (solid) and 10 kV m^{-1} (dashed).

The accumulation of particles per 8 hours is given in Table 6, both as number and area coverage.

Table 6. Surface accumulation rates

Concentration particles cm^{-3}	Diameter	Deposition velocity cm s^{-1}	Accumulation, # cm^{-2} per 8h	% surface area covered per 8h
10^5	10 nm	0.008	2.3×10^7	0.0018%
		0.08	2.3×10^8	0.018%
	100 nm	0.0008	2.3×10^6	0.018%
		0.01	2.9×10^7	0.16%

4.7.3 Coagulation

Coagulation of nanosized particles can be extremely fast. The time ($T_{1/2}$) it takes for halving the concentration of the original size monodisperse particles are given in Table 7 for unit density particles and concentration 1 mg m^{-3} (Preining, 1992). $T_{1/2}$ is inversely proportional to particle concentration

Table 7. Coagulation time constant for particle concentration 1 mg m^{-3} according to Preining (1992).

Particle size, nm	0.5	1	2	5	10
$T_{1/2}$, s	3.0×10^{-4}	2.2×10^{-3}	1.2×10^{-2}	0.12	0.7

5. Workplace exposure data

5.1 Introduction

There are currently no national or international consensus standards on measurement techniques for nanoparticles at the work place. Thus, the occupational hygiene community has been hesitant initiating comprehensive monitoring. Hitherto, most ultrafine particles have been quantified by one or several of the methods condensation particles counters (measures total particle concentration in a size range of typically 10-1000 nm), electrical mobility analyzers, electrical low-pressure impactor, and others.

Researchers from several European research institutes have proposed a measurement convention (BGIA, 2007) stating that

- Ultrafine particles should be quantified by number concentration and size distribution. This allows estimation of surface and volume distribution
- Mobility spectrometers and condensation particle counters can be regarded as reference instruments
- Single particle analysis can be performed by thermophoretic or electrostatic particle collection techniques for subsequent analysis e.g. by TEM/EDX.

Monitoring exposure by inhalation to nanoparticles presents some unique challenges.

- Most exposures will be in the form of aggregates. Size as measured by e.g. impactors or mobility analyzers cannot reveal the agglomeration state, and thus to which degree an agglomerate can break up into many smaller units in the lung fluids. Thus results of such measurements cannot be directly related to risk if particle number is a relevant measure of this risk. No simple measurement approach to meet this challenge is at hand
- High background concentrations of ultrafine particles are ubiquitous. Measurement methods thus must be able to distinguish between the nanoparticles in question and the background of nanosized particles. At present there are only two approaches available for separating between engineered nanoparticles and other particles of the same size range for use outside the research laboratories. One is by intelligent design of sampling strategies. The other is to collect particles on suitable substrates for later analysis in the laboratory using time consuming electron microscopy.

5.2 Ultrafine particles

In order to put exposure to engineered nanoparticles into perspective, exposures to ultrafine particles for some selected scenarios is presented.

In an engine machining and assembly facility 98% of the particles smaller than 1 μm were below 100 nm as estimated by using an optical particle counter in combination with a condensation particle counter. Ultrafine particle concentrations possibly attributable to metalworking operations ranged 250 000 to 750 000 particles cm^{-3} (Peters *et al.*, 2006). On the other hand only about 10% of the mass was found in particles below 100 nm in bronze foundry and welding (Schimberg and Ukkonen, 2003).

Kuhlbusch *et al.* (2004) found that bag filling in a carbon black producing facility was not a source of ultrafine particles. In the work areas of the reactor and pelletizer of three carbon black production plants Kuhlbusch and Fissan (2006) found that elevated ultrafine particle number concentrations with respect to ambient were related to nearby traffic emissions or to grease and oil fumes from maintenance activities, or in one of the plants to leaks in the production line, which allowed particulate matter to escape to the surrounding areas. The authors concluded that no carbon black is released in the reactor and pelletizing areas (as ultrafine or PM_{10}) from the closed production lines under normal operating conditions.

Thomassen *et al.* (2006) measured particle concentrations in an aluminium smelter. During anode change they found a strong number mode below 10 nm as well as a mode in the range 50-100 nm. The smallest mode could not be detected by transmission electron microscopy (TEM), and the authors hypothesized the particles were not stable under sampling or the vacuum in the TEM.

Concentrations measured by Ukkonen *et al.* (2005), Riediger (personal communication), and Möhlmann (2005) are summarized in Table 8. The measurements by (Wake *et al.*, 2002) during handling of high specific surface area carbon black, precious metal black and nickel powder, ultrafine TiO_2 , and of unwanted ultrafine particles (metal spraying and coating, welding, soldering, foundry fumes) are reproduced in Table 9. Figure 26 summarizes the results.

Table 8. Particle number and mass concentrations at industrial sites

Process	Number $\times 10^{-3}$ (GM) cm^{-3}	Median diameter nm	Mode nm	Mass mg m^{-3}	Reference
Plasma cutting §	40–800	40–60		0.3–1.3 (PM _{2.5} ,S)	Ukkonen <i>et al.</i> (2005)
Plasma cutting	40–230	140–180	120–180	4.2 (I)	Riediger (personal communication) and Möhlmann (2005)
Laser welding Aluminum	5 000–40 000		40–100	0.17–0.48 (I)	
welding	20–640	256–411	217–594	2.8–15 (R,P)	
Soldering	28–390	43–62	36–64	<0.76 (I,P)	
Cutting alu-minium, minimal MVF	10–260	30–111	15–131	<0.95 (I,P)	
Iron foundry	290–580	54–70	50–80	1.5–1.7 (I)	
Plastic die casting	20	45	23	<0.25 (R,S)	
Grinding metal	10–130	32–155	19–170	1.8 (I)	
Grinding granite	26–60	<10	<10	Up to 41 (I,P)	
Baking bread	5–640	55–83	32–109	0.3 (I)	
Airport out-door	26–700	<41	<45	0.07 (I,S)	

All measurements with SMPS: Scanning Mobility particle Sizer, except (§) made with ELPI: Electrical Low Pressure Impactor. I: Inhalable, R: Respirable, P: personal sample, S: Stationary sample. MVF: metalworking fluid.

Table 9. Number concentrations and particle sizes during handling of high specific surface area materials (carbon black, precious metal black, nickel powder), ultrafine TiO₂, and of unwanted ultrafine particles (metal spraying and coating, welding, soldering, foundry fumes). From Wake *et al.* (2002)

Type of industry	Outside Range $\text{cm}^{-3} \times 10^{-3}$	Workplace Range $\text{cm}^{-3} \times 10^{-3}$	Outside Number median, nm (GSD)	Workplace Number me- dian, nm (GSD)	Activity
Carbon black	649–3836	3.5–50	44 (3.2)	51–400 (2.4)	Bagging
Nickel powder	3.3–16	3.7–212	23 (1.9)	49 (3.3)	Bagging
Titanium dioxide	10–58	4.2–17			Bagging
Precious metal blacks	19–62	23–71			Sieving
Zinc refining	20–23	12–24	503 (5.3)	70 (2.2)	Sintering
Zinc refining	20–23	56	100		Casting
Plasma coating	2.3–8.0	2.8–905	41 (2.2)	587 (1.3)	Wire coating
Galvanizing	15–37	10–683	64 (2.0)	99 (2.1)	Galvanizing
Steel foundry	13–72	118–>500	46 (1.9)	66 (2.0)	Fettling
Welding	10–19	117–>500	53 (2.1)	179 (2.2)	MIG
Plastic welding	1.2–5.2	111–3766	31 (2.0)	37 (1.7)	Welding
Hand soldering	2.2–11	12–>500	41 (2.0)	72 (2.3)	Tinning

5.3 Engineered nanoparticles

5.3.1 Production and handling

Plitzko *et al.* (2006) have reported preliminary results from measurements in Germany under laboratory scale and small-scale industrial production and handling. They found that these activities did not significantly increase particle concentration above background.

The US National Institute of Occupational Safety and Health (NIOSH, 2005) has published a Health Hazard Evaluation Report on employee exposure to carbon nanofibres during various handling operations in laboratories of a university. The tasks monitored were chopping, transferring about ½ kilo of carbon nanofibres from outside a laboratory hood to a beaker for weighing inside the hood, transfer, and manually mixing carbon nanofibres with acetone. Measurements were made by stationary instruments, usually within less than one metre of any potential source of emission. Concentration of nanosized particles in the indoor background was less than outdoors. In terms of number (as measured by the Electrical Low Pressure Impactor) a slight increase was found for mixing above 400 nm, and above 500 nm for measurements made above the mixing vessel during mixing. A TEM analysis showed that the majority of fibres appeared as loosely bundled agglomerates.

5.3.2 Machining, wear, and degradation

One central question is if and to which degree machining, wear, and degradation sets free nanoaerosols or aerosols that, if deposited in the airways, have toxicological properties differing from those of the bulk materials they were made of. Data are virtually absent and only the following could be retrieved. NIOSH (2005) studied sawing operations in laboratories of a university. The tasks monitored were cutting carbon nanofibre composite materials with a water-cooled table saw. Measurements were made by stationary instruments, usually within less than one metre of any potential source of emission. In terms of number (as measured by the Electrical Low Pressure Impactor) a slight increase was found for wet saw cutting for particles above 400 nm.

In a diploma work at Chalmers University of Technology (Li, 2006) nanoparticle release from abrasive wear of a nanocomposite was studied. The nanocomposite was polypropylene with nanoclay (montmorillonite). The author concluded that there was no nano particle release from the composite from abrasive wear. However the level of detection was unclear. Combustion tests showed ten times higher particle number concentrations found for the nanocomposites than for the pure propylene material and for all particle sizes from 10 nm to 2500 nm. The author specu-

lated that this might be more due to the incomplete combustion of the nanocomposite than to the release of nanoclay particles.

5.4 Background concentration

One of the great challenges in assessing exposures to engineered nanoparticles is that the ubiquitous combustion and evaporation/condensation processes can generate high background concentrations. This often occurs in synchrony with activation of the potential nanoparticle sources. An example of the importance of keeping track of other sources is given by Kuhlbusch *et al.* (2004) who showed that a butane gas fork lift can be a dominating source of ultrafine particles during bag filling in a carbon black producing facility. Peters *et al.* (2006) found that while ultrafine particle concentrations in an engine machining and assembly facility possibly attributable to metalworking operations ranged from 250 000 to 750 000 particles cm^{-3} , the concentrations in supply air heated by direct heating natural gas burners were above 1 000 000 particles cm^{-3} .

6. Specific exposure scenarios

6.1 Introduction

Production of engineered nanoparticles is a highly sophisticated process. It is likely that air contamination will be low and many materials will only be manufactured in kilogram quantities in the nearest future. Experimental and pilot-scale production are considered important scenarios and exposure assessment can assist the pioneer enterprises in identifying and managing their exposure risks. It is possible that some pioneer manufacturers are unaware of, or have limited data on health risks.

One aim of the project thus was to collect examples of specific nanoparticle exposure scenarios. The project group has had contact to several enterprises judged to be of potential relevance to the project. It was realized that while there are many enterprises on the lists of those interested in engineered nanoparticle technology, few industries actually manufacture or use engineered nanoparticles. This has greatly reduced the number of exposure scenarios that could be collected. This is not unique for the Nordic countries. According to colleagues in other European countries their situation is similar. Some potential candidate enterprises were taking part in the NANOSAFE 2 project¹³. As a consequence, they preferred to publish exposure relevant information in future NANOSAFE 2 reports. As anticipated at the formulation of the present project, other enterprises were reluctant to disclose exposure related information in a form useful for the project. The available data for characterizing exposure scenarios is thus variable and limited in extent. General conclusions regarding exposure risk thus cannot be drawn.

6.2 Welding

The welding industry is a major player in worldwide manufacturing and encompasses a vast number of different welding processes. Many of these are similar to the thermal processes used for production of engineered nanoparticles. Welders are exposed to aerosols which are formed primarily through homogeneous nucleation of element vapour followed by competing growth mechanisms such as coagulation and condensation. Individual particles freshly formed near the welding arc are mainly spherical with diameters ranging from few nm to more than one μm dependent on welding methods. At National Institute of Occupational

• ¹³ <http://www.nanosafe.org/>

Health in Oslo, some preliminary particle size distribution measurements using a TSI SMPS instrument have been made for some common welding methods (see Figure 27, results supplied by Yngvar Thomassen). It is obvious from these preliminary data that the welding fume generated be considered as a nanoparticle containing aerosol.

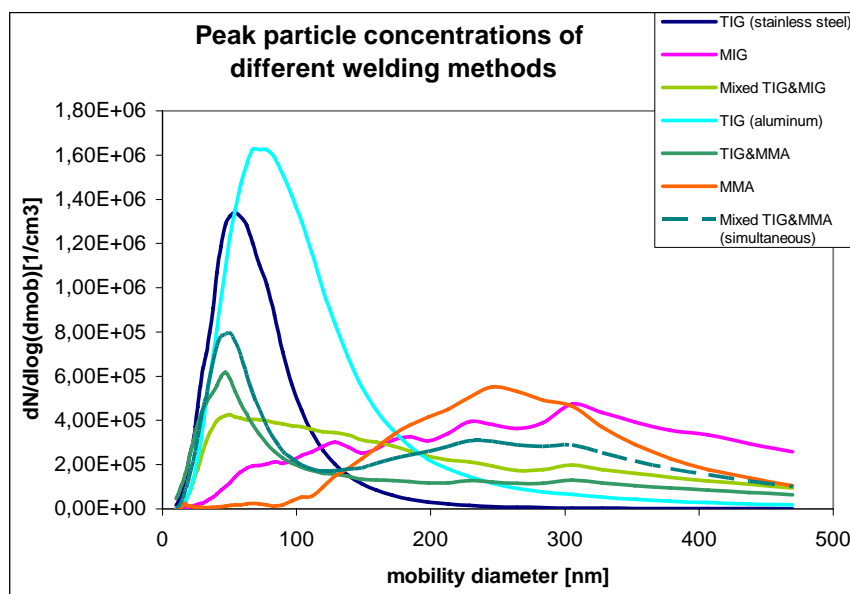


Figure 27 Peak particle concentration of different welding methods (results supplied by Yngvar Thomassen).

6.3 Exposure to amorphous SiO₂ fume in smelters

In collaboration with National Institute of Occupational Health, Oslo, Elkem ASA has performed an exposure assessment of workers in 7 smelters producing silicon, ferrosilicon and micro silica¹⁴. In total 49 personal full-shift respirable air samples have been analysed by FTIR for amorphous SiO₂. The highest arithmetic average concentration was found among the furnace tapping operators (3.5 mg m⁻³, n=27) in comparison to the micro silica recovery department (0.35 mg m⁻³, n=5). Although the average individual particle diameter in the freshly formed fume is about 150 nm, the fine particles tend to agglomerate in the recovery process to much coarser particles. Thus the highest exposure levels among workers are found in the furnace department and not during handling of the recovered fume.

• ¹⁴ Siri Hetland, STAMI-report-2005

6.4 Paint manufacturing

Conventional paint was manufactured by mixing solid and liquid ingredients in large (5 m³) tanks (dissolvers). The solid materials were added manually from “big bags” handled with a crane or from bags that were emptied into the dissolver manually. In the future engineered nanoparticles may replace some of the fillers, pigments, and binders. If they were to be added as dry powders or granules and with unchanged technical controls, nanoparticle exposure may occur during bag emptying and discarding, during cleaning operations, and during inspection e.g. manual temperature control (Figure 28).



Figure 28. Temperature reading in dissolver.

6.5 Paint and lacquer sanding

The paint and lacquer industry has no regular production using engineered nanoparticles as raw materials. To insure the safety of potential future products using engineered nanoparticles the Danish National Research Centre for the Working Environment is conducting a research project in cooperation with the Danish paint and lacquer industry. The project will provide quantitative data on emission rate, size distribution, and toxicological properties of aerosols generated during sanding with electrical hand tools of paints, UV hardened lacquers, and fillers containing nanoparticles.

6.6 Textile manufacturing

Through a high-technology project Fibertex A/S will utilise nanotechnology and nanoparticles for manufacturing nonwovens. Currently the project has not yet resulted in large-scale test productions and particle exposure data during production of non-woven textiles were not available. However, the materials are planned to be produced using the established spunmelt (Figure 29) and/or non-woven “felt” (Figure 30) production technologies (personal communication Fibertex). The production line is not enclosed. In both systems, the textile is produced from granules. Incorporation of the nanoparticles is anticipated to occur by adding them in functionalized form from a liquid master mix. The spunbond-meltblown technology is an integrated one-step process ranging from resin extrusion to lightweight fabric production.¹⁵

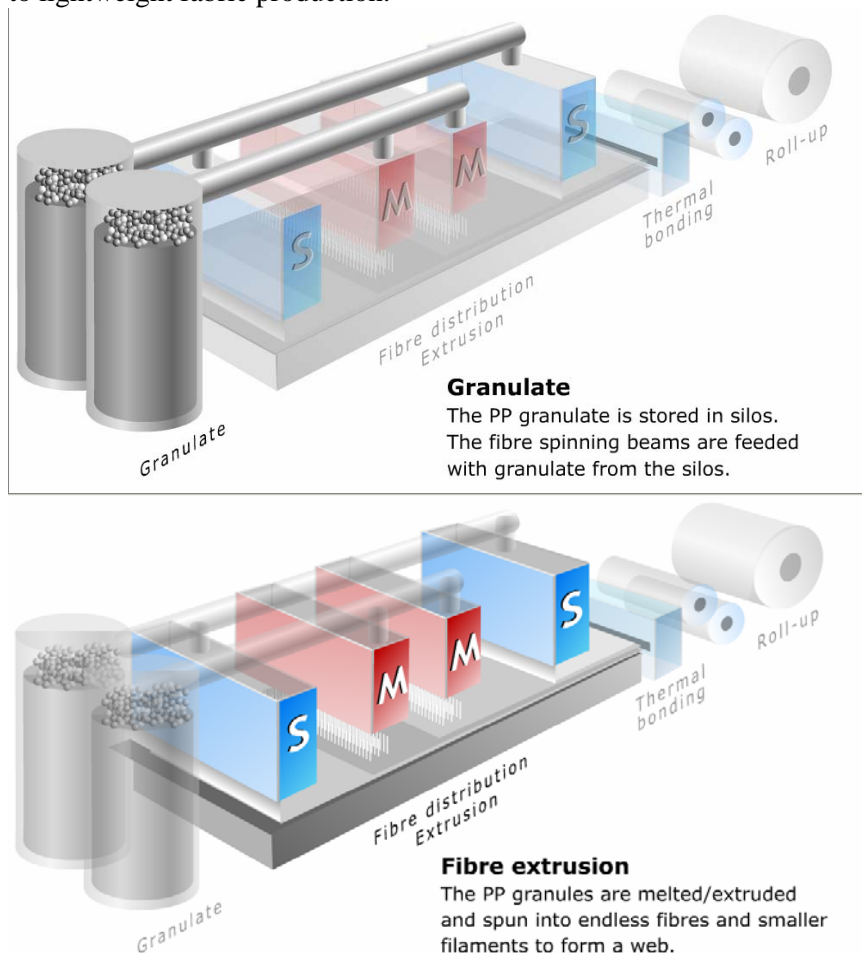


Figure 29. General production line for spun melt non-woven textiles.¹⁶

- ¹⁵ <http://www.fibertex.com/da-DK/technology/spunmelt/Pages/default.aspx>
- ¹⁶ <http://www.fibertex.com/en-GB/technology/Spunmelt/PublishingImages/Spunbond.swf>

The dry-laid needlepunch production technology is based on a two-step process. First, polypropylene resin is extruded into fibres. Secondly, these fibres are carded and needlepunched and then bonded thermally to form nonwovens.¹⁷

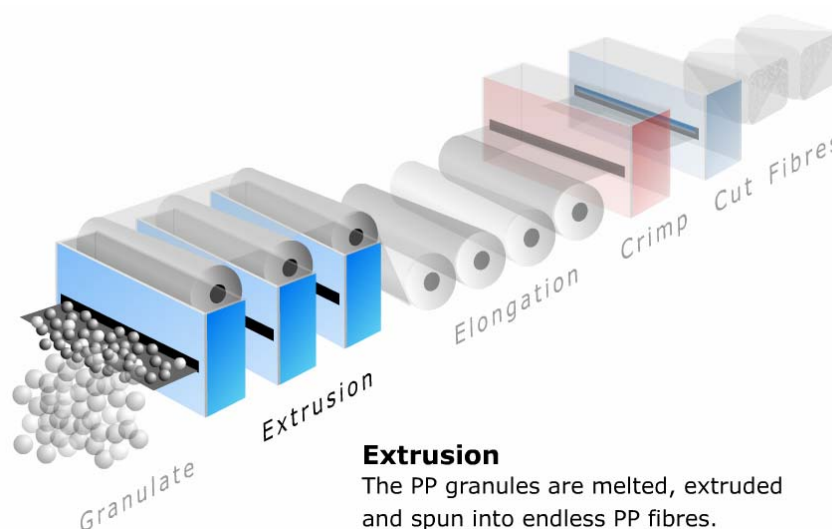


Figure 30. General production line for non-woven needlepunch.¹⁸

The production technologies employ elevated temperatures to produce the polymer melt. Even though production occurs in non-enclosed environments direct exposure during production is expected to be low. The melt-technology is thought to retard liberation of the engineered particles during production. Elevated particle exposures are apparently not observed during production using conventional pigments.

There is no information on potential exposure to nanoparticles during use of nanoparticle-doped nonwovens and during waste treatment.

6.7 Spraying (surface treatments)

Currently nanoparticle-based nanofilm products or penetrative surface treatments (particles and chemicals that enter at least the outer surface layer of a material) receive increased attention in industry. Most of the current products are applied using pumps or pressurized cans or alternatively applying the chemicals with a soaked cloth. When scaling up the use of these products for application in e.g., the textile, paint and lacquer treatment or construction industries, these dispensing methods are no longer applicable. Professional application of large amounts of surface treatment products for building walls is currently conducted using compressed air dispersion or electro-spraying (Figure 31). Application of the

• ¹⁷<http://www.fibertex.com/en-GB/technology/Needlepunch/Pages/default.aspx>

• ¹⁸<http://www.fibertex.com/en-B/technology/Needlepunch/PublishingImages/pptofibers.swf>

chemicals to horizontal surfaces may be by mobile units spraying or dispensing the chemicals directly onto the surface or vehicles (Figure 31). However, choice of method for industrial scale dispensing of the nanoparticle doped or nanoparticle forming chemicals will depend on the efficiency of the treatment obtainable with a given method of application. Currently such information and consequently corresponding exposure data do not exist.



Figure 31 Two potential surface treatment scenarios for large scale applications of surface treatments.

6.8 Nanoscale surface coating

Surface coating such as physical vapour deposition and similar may potentially generate nanoparticles. However, such processes are generally performed in closed chambers and with high vacuum preventing release of particles.

6.9 Production of metal oxide nanoparticles (laboratory scale)

The liquid flame spray (LFS) method was used in a research laboratory to produce metal oxide nanoparticles. The generated particles were collected as a powder. Production lasted 1 hour per day, during which period about 100 mg powder was produced. Potential inhalation risks were identified to be in the production room and during handling and collecting the powder from the collector device. Air concentrations were measured using a condensation particle counter and electrical low-pressure impactor. The results showed that concentrations could exceed 10^6 particles cm^{-3} during spraying, up to 10 mg m^{-3} .

6.10 Handling of carbon nanotubes

Handling of carbon nanotubes at SAAB, Sweden (and Bodycote Värmebehandling AB) is on a research and laboratory scale. In lack of toxicological, and occupational and industrial hygiene data the precautionary measures taken are to handle the fibres as asbestos. It was found that carbon nanotubes as dry powders from different suppliers differ in their properties, for example apart from size distributions their state of agglomeration and bundling differs. This may have significance from an occupational exposure perspective.

6.11 Laboratory handling of nanopowders

Particle concentration in the breathing zone of laboratory technicians was monitored using a TSI Fast Mobility Particle Sizer. No increase relative to background was discernible during weighing or sonication. When cyclones that had been charged with goethite or bentonite were cleaned in a fume cupboard using pressurized CO₂ a short (5 s) peak was detected in the breathing zone. The peak concentration of nanosized particles was about 10⁶ particles cm⁻³ and about 30 times less for particles above 100 nm. In a later aerosol chamber test the pressurized CO₂ was activated, and a similar peak was observed. It thus is likely that the peak of nanosized particles observed during cleaning of the cyclone was not due to the resuspended particles, but was generated by the release of pressurized CO₂.

6.12 Failure testing and demolition of carbon nanotube-doped concrete

One of the potential uses of the extraordinary tensile strength of carbon nanotubes (CNT) is in reinforced concrete. This suggests future occupational CNT exposure scenarios such as during drilling and cutting concrete and during demolition. In research laboratories developing these new types of concrete, potential exposure can take place during preparation of concrete and e.g. failure testing.

The National Research Institute has in collaboration with Lawrence Technical University (MI, USA) initiated a feasibility study of the production and particle release during failure (mechanical testing) of CNT-doped Portland cement concrete (PCC) specimens. Figure 32 shows the laboratory-scale production and testing of the CNT-doped mortar samples. Dispersion of the CNT in water before mixing was considered to result in the lowest exposure risk during CNT-PCC production. Even though some research groups successfully have worked with dry powders, the traditional dry-mixing method was considered to be inadequate

for application of CNT's in the cement/concrete industry. The risk from dry mixing of CNT is difficult to assess, because the dustiness and agglomeration of CNT is not well understood.

Analysis of the particle release from CNT-doped PCC is relevant for estimating the potential secondary exposure to workers during demolition and recycling as well as accidental mechanical failure of structures. Destructive testing was completed in a closed particle sampling and monitoring chamber built around the mechanical compression test facility, Figure 32.

Preliminary results from the study have shown that both CNT-doped PCC and control PCC may release particles below 30-40 nm, during mechanical failure. However most of the sub-micrometer particles released during the mechanical failure occurred in a size mode around 200 nm, Figure 33. The results suggest that release of particles in both size ranges during testing of CNT-doped PCC may be a higher than for the control PCC. Noteworthy, the total number concentration immediately after specimen failure was generally about 10 times higher (10^4 particles cm^{-3}) when testing the CNT-doped PCC in the chamber than the PCC controls (10^3 particles cm^{-3}).

Relatively large quantities of coarse particles were also released in the mechanical tests occasionally exceeding 500 particles cm^{-3} as measured with the Aerosol Particle Sizer 3321 (TSI Inc.). These coarse particles have a typical peak mode around 1 μm and a geometric mean aerodynamic diameter around 1.3 μm (not shown).

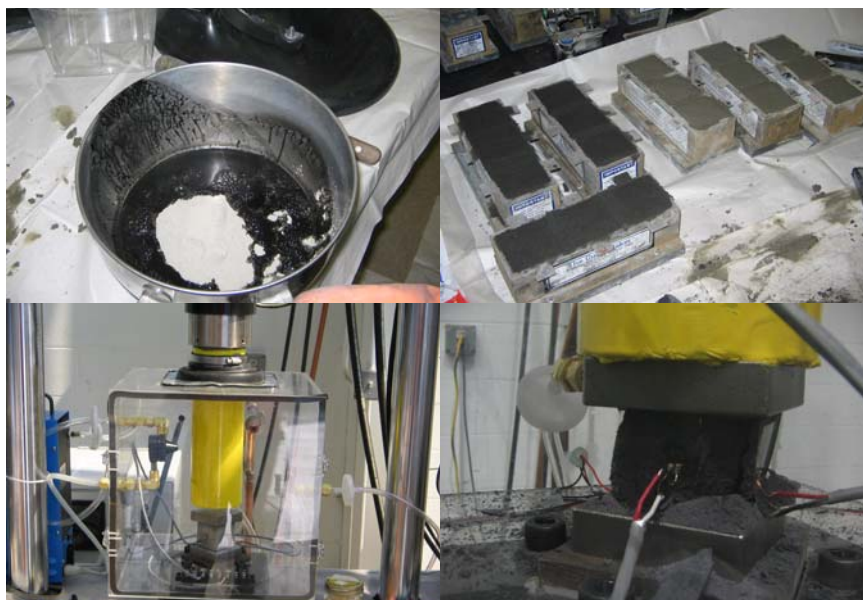


Figure 32. Images from the CNT-PCC feasibility study showing top left) the production of the cement mortar based on liquid dispersed CNT, top right) molding and bottom left) the chamber for analysis of mechanical performance and bottom right) illustration of the deformed mortar cube at the end of studies of mechanical strength and associated particle release.

Even though it is a tempting conclusion that the higher particle concentrations generated during tests with CNT-doped PCC may be caused by release of individual CNT's or bundles thereof during fracturing, this may not be the case. It may be caused by several other factors such as a potential lower cement hydration or micro- to nano-structural heterogeneity. This will be further investigated during the project.

These findings could suggest that nanoparticles will be released at worksites, during drilling or cutting concrete and during demolition and recycling.

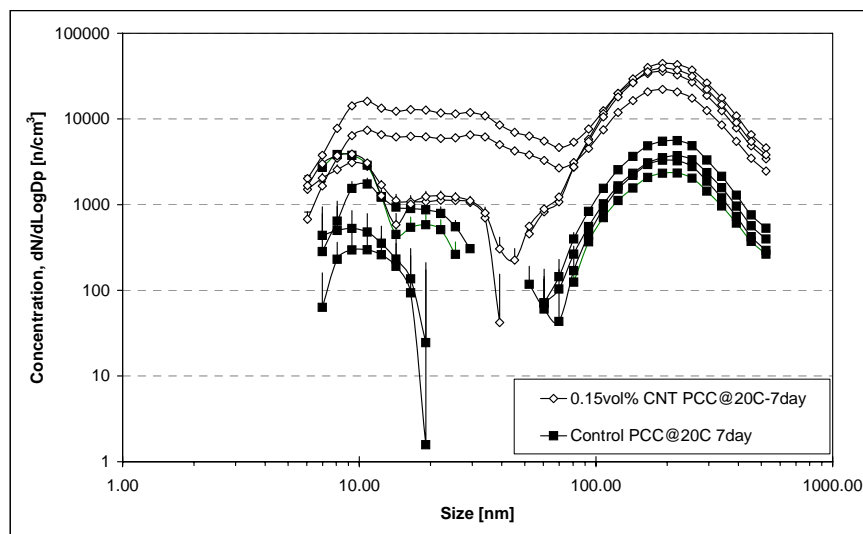


Figure 33. Examples of particle number size distributions at peak concentrations for particles generated during mechanical compressive failure testing of normal Portland clinker cement (Control PCC) and PCC doped with 0.15vol% CNT. Samples were cured for 7 days at 20 °C. Data were corrected for background concentrations measured before onset of failure.

6.13 Ski waxing

Ski waxes are often based on polymers of fluorocarbons. Many of these waxes are powders with particles with nanoscale surface structures. These ski waxes are extensively and increasingly used and exposure to these products does occur. Professional ski waxers both in cross country and down hill skiing are occupationally exposed to these compounds. Their workplace is ambulating from place to place and the work is often carried out in provisional workplaces that are not adapted for this kind of work. There also is a large group of ski waxers who work as volunteers in non-profit sports clubs for youngsters. Many amateur skiers wax their skis themselves and can therefore also be exposed.

6.14 “Consumers” exposed to sprays

“Nanofilm”-producing pumps and spray cans are primarily intended for the consumer market, but can also find application in e.g. furniture, textile, and lacquering retail and production companies. Funded by Nano-Cover A/S the National Research Centre for the Working Environment is conducting a risk assessment of selected products. Preliminary data have been obtained from tests in a 0.2 m³ stirred aerosol chamber. Application of a surface treatment product using a spray generated a particle size distribution with one mode at 10–15 nm and another at 75 nm. Slightly larger nanoparticles with a mode at 34 to 49 nm were generated using the pump version. Concentrations for a single ~1 sec spray resulted in up to 2.5×10⁵ particles cm⁻³. Using the pump, one stroke generated a total concentration of about 10³ particles cm⁻³ (Figure 34).

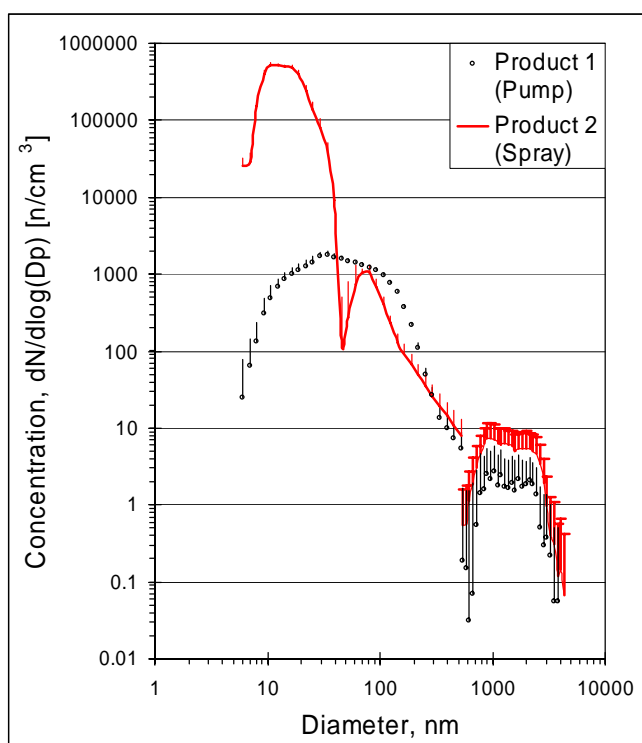


Figure 34. Size distribution of aerosol generated during application of two different surface treatment products. Particle size concentrations were measured using a Fast Mobility Particle Sizer Model 3091 (5.6–560 nm) and a time-of-flight Aerosol Particle Sizer Model 3321 (520–20,000 nm), both from TSI.

In both product types only a small fraction of the particles were larger than 200 nm showing that these products are truly based on nanoparticle technology. The preliminary results show that application of spray-on surface treatment products generates aerosols in the nanoparticle range. They also show that the method of application (and possibly also the type

of product) has a large effect on particle concentration. The true number of nanoparticles may be higher as a fraction of the generated droplets may contain several individual nanoparticles. This will result in agglomerates of nanoparticles after the liquid has evaporated and complicates evaluation of the exposure. It should be noted that these experiments were conducted in an aerosol chamber and therefore that the concentrations may not be indicative of personal exposures during use.

7. Occupational exposure during entire life cycle

Nanotechnology and Life Cycle Assessment was the topic of a workshop organized by the US Environmental Protection Agency/Woodrow Wilson International Centre for Scholars and the European Commission (Karn and Aguar, 2007). The workshop quoted a literature search by Lekas (2005) to document that due to the newness of the field, only seven life cycle assessments involving nanotechnologies had been published. These were:

- Automotive application
 - Clay polypropylene nanocomposite for light-weight construction
 - Nanoscale platinum-group metal for catalysts
- Chemical application
 - Nano-varnish
 - Powder-coating technology
- Electronics
 - Semiconductor crystals and carbon nanotubes for displays
 - Desk-top computer displays
- Energy
 - Quantum dots and semiconductor crystals in light-emitting diodes

The project group could not meaningfully assign likelihood and intensity of occupational nanoparticle exposure for representative exposure scenarios during a life cycle. The reasons were

- The present project has demonstrated that the amount of information on occupational exposure scenarios and quantitative exposure information for engineered nanoparticles in the air is very limited
- The combined set of all conceivable occupational exposure scenarios during a life cycle is immensely broad
- There will be fundamental differences between exposure scenarios where engineered nanoparticles are manufactured by workers trained in handling engineered nanoparticles and final product utilization, where users may not be aware of any special requirements for dust control.
- Unknown changes in societal behaviour in using nanoproducts

As a consequence, the group only prepared a list of some “interesting scenarios”.

Surface treatment of textiles with engineered nanoparticles leads to reduced need for washing, reducing use and environmental discharge of detergents. On the other hand, there will be a constant need for maintaining the surface treatment with engineered nanoparticles. This task will probably be carried out by specialized workers, thereby increasing potential exposure but for a limited group of persons. Similarly for glass treatment where durability is low, needing frequent re-application.

Engineered nanoparticles in paints will increase the life time of the painted surface, reducing paint consumption and causing fewer man-hours of exposure.

Recycling and handling of problem waste could become as complex as for to-days electronic equipment.

Some engineered nanoparticles are designed to react with the matrix thereby loosing their original properties.

Demolition of concrete

- Nanosilica based. While nanosilica particles have reacted with the matrix, the problem will probably not be liberation of these nanoparticles, but the increased strength which will render constructions harder to pull down.
- CNT enforced. The results presented in section 6.12 could suggest that generation of nanosized particles should be evaluated for such scenarios.

Engineered nanoparticle reinforced composites. If the materials are organic, they can be incinerated.

Use of wear resistant surfaces in e.g. machine and pump units will reduce the amount of e.g. hard metals and prolong life-time of the product. This will have implications for the number of workers (normalized to number of units) exposed during manufacturing of the traditional units, while posing potential new exposures during manufacture of the surfaces and later maintenance, repair and recycling.

Car catalysts: there is a potential for releasing nanoparticles into the environment upon heating.

Waste handling and sorting

- If materials or products containing engineered nanoparticles are handled as ordinary waste special attention should be paid to situations where nanosized particulate material becomes concentrated such when collecting batteries and electronics.
- Car catalysts will probably be treated as toxic metals corresponding to the elemental composition of the catalyst.

8. Quality of information in MSDS

8.1 Introduction

Material safety data sheets (MSDS) are important for safe handling of chemicals at the work place. The EU has legislated the requirements and instructions for MSDS in Commission directive 91/155/EEC of 5 March 1991 which was amended in 2001 (Com. Dir. 2001/58/EC). The design of MSDS is similar, although not identical, in countries outside the EU. Classification and labelling as “hazardous” has many consequences for the compound in question, e.g. regarding exposure control, first aid measures, storage, and transportation requirements.

Within the EU classification and labelling is regulated (Dir. 67/548/EC and 1999/45/EC). A UN initiative, together with OECD and EU, has resulted in a Globally Harmonised Classification System (GHS), which contains harmonised criteria and hazard communication elements.

The responsibility for the information in the MSDS lies on the supplier who places the product on market and there is no public notification or requirements of quality control. It may therefore be expected that the accuracy and quality of the information varies. A few reports have warned about deficiencies in the information in MSDS (Bernstein, 2002; Kopstein, 2006; Frazier *et al.* 2001; Welsh *et al.* 2000). Also at the 1st International Symposium on Nanotechnology and Occupational Health, in Buxton, UK, October a workshop on regulatory implications Kuempel and Aitken (2004) concluded that the adequacy of labelling and of MSDS should be considered, in particular whether data on particles of larger size or different form or composition is relevant to the nanomaterial.

There is incomplete information of the toxicity of nanoparticles and major gaps in the knowledge necessary for risk assessment (SCENIHR, 2006). These gaps include nanoparticle characterisation, the detection and measurement of nanoparticles, the dose-response, fate, and persistence of nanoparticles in humans and in the environment, and all aspects of toxicology and environmental toxicology related to nanoparticles.

As part of the project the quality of MSDS for products available on the market was thus examined. The MSDS to be studied were selected from a range of nanomaterials within five categories.

8.2 The MSDS

Some of the MSDS were obtained from producers of nanomaterials in the Nordic countries that were known to us. Other materials and suppliers were identified by the Google search engine and the MSDS were usually downloaded from the suppliers' websites. The MSDS were retrieved between June 2006 and January 2007. Materials were chosen with primary particles sizes as small as possible, to reflect a range of properties. Some of the MSDS were provided primarily for the marketing in the USA and Canada. The materials categories were:

- Silica (8)
- Titanium dioxide (4)
- Zirconium dioxide (2)
- Carbon nanotubes (11)
- C₆₀ Fullerenes (2)
- Cadmium-based quantum dots (3)

A check list was constructed based on the instructions "Guide to the compilation of safety data sheets" in the annex of the EU Commission Directive 2001/58/EC. Each MSDS was evaluated by three toxicologists following this check list. Published data on toxicology was used to evaluate the toxicological information.

8.3 Results in brief

In general the identification of the substance and the identification of the company were satisfying. Many MSDS however lacked emergency telephone number. In general, the compositions were well described, as far as the toxicologists could judge. However for many materials the EINECS number was missing, mainly in MSDS that appear were designed primarily for non-EU countries. R-phrases should be given in under the identification. Only in few cases the R-phrases were stated in this section although in other cases they were listed under the heading "Toxicology". Within the groups there was inconsistency in listing of R-phrases. For instance for carbon nanotubes a few MSDS indicated labelling symbol "Xi" for irritant or "T" for toxic and R-phrases R36/37 and R36/37/40 but in most instances there were no R-phrases listed in the MSDS.

Classification and labelling were many times missing from the MSDS, because there were no test results available for the substance or compound in question. Toxicological testing results were in few cases available and mainly concerning acute toxicity and irritancy (e.g. for silica and titanium dioxide, car MSDSs), but the references were missing. One reason could be that

- particle size is not one of the characteristic which needs to be provided
- a substance/compound does not need to be retested if the particle size changes to nano level or if the material contained nanoparticles.

In some cases “nano” was indicated in the commercial name of the material. Most of the carbon nanotube materials were identified as graphite.

First aid and fire-fighting measures were provided. In some cases the toxicologists were uncertain about the efficacy of the recommended first aid measures, due to the lack of information in the toxicity testing results and classification.

The quality of the proposed handling, storage and exposure controls/personal protection varied much between the MSDS even for materials of the same character. In some there was detailed recommendation on engineering controls, personal protection. E.g. some MSDS recommended respiratory protection with specific (standard) filter types that are effective for protection against ultra-fine aerosols. In other MSDS the instructions for recommendations for handling, storage and exposure controls/personal protection were very brief.

Also the descriptions of physical and chemical properties, conditions and materials to avoid were very different between the MSDS. Some MSDS had a description with one or two statements, whereas others had many properties described. For the carbon-based materials the possibilities of fire, reaction with strong oxidants and generation of carbon di- and monoxide were described. In the instructions in the EU commission directive there is no recommendation for giving a dustiness value and in no MSDS was dustiness described, although sometimes other information in the MSDS indicated that the materials were dusty.

Some MSDS had well described lists of exposure limit values and toxicity tests. Even for similar materials however the described toxicological properties varied.

There was very little ecological information in the MSDS. For some materials it was recommended that the materials should be disposed of by incineration under local regulations.

8.4 Discussion

Only a few of the MSDS were available in the Nordic languages. The identification was generally satisfying, although quite many were not identified as nanomaterials. However such identification is not required by current legislation. In some instances the CAS number was missing and in many instances the EINECS identification. C₆₀ fullerenes have a unique CAS number but are not listed in the European chemical substances information system and do therefore not have an EINECS num-

ber. A cautious approach might suggest C₆₀ fullerenes be treated as new chemicals.

Usually the carbon nanotubes were described as graphite. Recent data demonstrate that carbon nanotubes are inflammatory when deposited in the lung, and cause persistent pathological changes of granulomas and fibrosis (Lam *et al.*, 2006; Donaldson *et al.*, 2006). The potency for the toxic effects appears to be greater than quartz in several investigations. It may therefore be misleading to describe the toxicity of carbon nanotubes as the same as graphite in view of current scientific data.

Also for nanomaterials made of nanocrystals containing cadmium, selenium or tellurium components, the toxicity in the MSDS was based on data from larger particles containing these elements, and not on these nanosized homologues. In some cases the MSDS states that the toxicity may be more or less compared to the larger corresponding particles, thus caution is encouraged when working with these materials.

In general the compounds/materials were practically not tested, and if so, many times for acute toxicity only. Irritancy was referred to in some. When there are no tests available, this means no classification and therefore no consequences for e.g. transportation and one could ask, if the "First aid" measures are OK. On the other hand, if one reads the "First aid" instructions one could come to a conclusion, that some hazardous properties are suspected.

It is suggested in the EU commission directive 2001/58/EC that it may be necessary to mention hazards, such as dustiness, which do not result in the classification, but may contribute to the overall hazards of the material. Because even high number concentrations of nanoparticle aerosols are invisible and the particles have the potency of being effectively deposited in the lower respiratory tract it could be argued that dustiness is an important parameter similar to the vapour pressure which is commonly described in MSDS for volatile organic compounds. A description of dustiness would be an important instrument in work place risk management. It was not described in the MSDS that nanoaerosols may have unique sedimentation and diffusion properties. However in some instances the recommendations on exposure control and personal protection were satisfying for nanoaerosols.

9. Trends in uses of nanoparticles

The global manufacturing output of nanoenabled products will raise from 30 billion US\$ in 2005 to 2.6 trillion US\$ in 2015. Large production volumes can be expected in cosmetics, textiles, coatings, and paints. Over the next five years a growth in use of nanoparticles is foreseen in relation to production of fuel cells, solar cells, and smart surfaces (Friedrichs and Schulte, 2007).

The Danish Ministry of Research, Technology, and Development (2004) has identified seven prioritized areas for development and application nanotechnology. One area is “nanomaterials with new functional properties”. Some examples are listed in Figure 35.

<div> <div>NANO TF</div> <div>Statements on future possibilities of nanotechnology</div> </div>		Period in which it is estimated the statement will become a reality			
Statement no.	Development stages are described using certain traditional, international definitions: <u>Development</u> : to reach a defined technological goal or complete a prototype. <u>Practical application</u> : the first practical application (often in a niche market) of a new product or a new process. <u>Wide application</u> : achievement of a significant market position by a new product or a new process.	Before 2010	2011-2015	2015-2020	2021-2025
	Nanomaterials with new functional properties				
26	Practical application of alloys or ceramic materials that crystallise with very small grain size (high strength and good workability) for high-value products, from the micro to the macro scale, from implants to sports equipment.				
27	Development of nanocomposites which are stronger, and have better thermal stability and chemical resistance, than pure polymers. Improvements in corrosion resistance, sound absorption, consolidation of manufactured pieces and recyclability.				
28	Practical application of woven and non-woven textiles made from polymer fibres in the textile and hygiene industries.				
29	Development of new types of coatings with built-in functions, achieved by building in a chemical functionality, through nanoparticles, or through a nanostructured topology.				
30	Practical application of block copolymers for the development of self-repairing surfaces (the material itself ensures that it is the correct functional block that is exposed).				
31	Practical application of nanoporous materials as filters in the food and drink industry.				
32	Development of thermoelectric materials with radically improved properties for cooling and energy production, based on nano-sized structures.				

Figure 35. Examples of development and application nanotechnology, from Danish Ministry of Research, Technology, and Development (2004).

Traditional producers of bulk powders are likely to manufacture products with ever decreasing mean particles size, i.e. having an increasing fraction of particles in the ultrafine size region. Major uses of engineered nanoparticles can be expected for enhancement of “old” materials, such

as use of carbon nanotubes in producing high performance sports gear and scratch resistant paints.

Engineered nanoparticle production in the Nordic countries is expected to remain small on a global scale. However, there can be niche production of functional nanoparticles, e.g. in relation to fuel cells and osmotic membranes.

The trend in the construction industry is particularly interesting because of its size both in number of employed persons and consumption of raw materials, the large crowd of do-it-yourself persons. A report on nanotechnology and construction (Mann, 2006) has identified the following nanoparticle based raw materials

- Silica. It is already in general use for improving mechanical properties and durability of concrete, see also section 2.5.2.
- TiO₂ (anatase). Introduced either in the building matrix or surface coatings the photo (solar-UV) catalytic action breaks down contaminants thereby potentially facilitating de-contaminating e.g. soiled facades by rain and reducing gaseous polluting indoors or in nearby air-spaces outdoors.¹⁹
- Carbon nanotubes. Improves the mechanical properties of concrete, see also section 6.13.

The paint and lacquer industry, already using ultrafine particle based raw materials expects a large increase in use of engineered nanoparticles.

Many future methods for production of engineered nanoparticles are expected to be based on production in liquids. The technological advantage will be e.g. better control of the properties, such as reproducible size distribution and agglomeration/aggregation. From a health point of view the advantage will be elimination of the need for down-stream users to handle dry materials.

• ¹⁹ Project supported by European Commission, see <http://www.picada-project.com>

References

- BAuA. (2006) Easy-to-use workplace control scheme for hazardous substances. <http://www.baua.de/nz-18306/en/Topics-from-A-to-Z/Hazardous-Substances/workplace-control-scheme.pdf>
- Balazy A, Podgorsky A, Gradon L. (2004). Filtration of nanosized aerosol particles in fibrous filters. I Experimental results. *Journal of Aerosol Science*, 35(Supplement 2): 967-968.
- Balazy A, Toivola M, Reponen T, Podgorski A, Zimmer A, Grinshpun SA. (2006). Manikin-Based Performance Evaluation of N95 Filtering-Facepiece Respirators Challenged with Nanoparticles. *Ann Occup Hyg*, 50(3): 259-269.
- Bernstein JA. (2002) Material safety data sheets: are they reliable in identifying human hazards? *J Allergy Clin Immunol*;110:35-38.
- BGIA. (2007) Ultrafine (Aerosol)-Teilchen und deren Agglomerate und Aggregate. <http://www.bgiaarbeitsmappedital.de/schnupperdokument.php?download=1>
- Bohgard M, Anderber MT, Ekholm A.-K. (1994) Source characteristics of emitted aerosol in the size range 0.02 to 10µm at pigment handling in dye manufacturing. *J Aerosol Sci* 25 (Suppl.1): S461-S462
- CEN (2006). EN 15051 Workplace atmospheres – Measurement of the dustiness of bulk materials – Requirements and reference test methods. European Committee for Standardization. Brussels.
- Cherrie JW, Schneider T, Spankie S, Quinn M. (1996) A new method for structured, subjective assessments of past concentrations. *Occupational Hygiene* 3:75-83.
- Cherrie JW, Soutar A, Tran L, Cowie H. (2004) Variability and uncertainty in chemical exposures for regulatory assessments. IOM Report TM/04/04. <http://www.iom-world.org/research/iomreports.php#IOMResearchReports>
- Christensen FM, de Bruijn JHM, Hansen BG, Munn, SJ, Sokull-Klüttgen B, Pedersen F. (2003) Assessment tools under the new European Union chemicals policy. GMI 41. 2003;1-19.
- Commission directive 2001/58/EC, Official Journal L 212/24 2001, P. 24–33.
- Commission directive 91/155/EEC, Official Journal L 076, 22/03/1991 P. 0035-0041
- Danish Ministry of Research, Technology, and Development (2004) Teknologisk fremsyn om dansk nanovidenskab og nanoteknologi <http://teknologiskfremsyn.dk/download/91.pdf> .
- Deer WA, Howie RA and Zussman JU. (1966) An introduction to rock-forming minerals. Longman Scientific & Technical, England.
- DIN (2006). DIN 55992-1. Determination of a parameter for the dust formation of pigments and extenders – Part 1: Rotation method (in German). DIN Deutsches Institut für Normung. Beuth Verlag, Berlin.
- Donaldson K, Aitken R, Tran L, Stone V, Duffin R, Forrest G, Alexander A. (2006) Carbon nanotubes: a review of their properties in relation to pulmonary toxicology and workplace safety. *Toxicol Sci* 92:5-22.
- Elkem Materials (2007) http://www.concrete.elkem.com/hits/internet.nsf/framesettopmenu?read-form&id=materialseng&full=full&lo=konsern_ny
- Endo Y, Alonso M. (2001) Physical Meaning of Specific Cake Resistance and Effects of Cake Properties in Compressible Cake Filtration. *Filtration & Separation* 38(7):42-46.
- Fibertex (2007). <http://www.fibertex.com/en-GB/news-and-events/Press/News/Pages/DanishHighTechnologyFund.aspx>

- Frazier LM, Beasley BW, Sharma GK, Mohyuddin AA (2001). Health information in material safety data sheets for a chemical which causes asthma. *J Gen Intern Med* 16:89-93.
- Friedrichs S, Schulte J. (2007) Environmental, health and safety aspects of nanotechnology—implications for the R&D in (small) companies. *Science and Technology of Advanced Materials* 8:12–18.
- Hakim LF, Portman JL, Casper MD, Weimer AW. (2005) Aggregation behaviour of nanoparticles in fluidized beds. *Powder Technol* 16:149–160.
- Haldor Topsoe (2007) <http://www.topsoe.com/site.nsf/all/BNN-5PFJAE?OpenDocument> Accessed 2007-07-05 .
- Hamelmann F, Schmidt E. (2004) Methods for Characterizing the Dustiness Estimation of Powders. *Chemical Engineering & Technology* 27(8):844-847.
- Heim M, Mullins BJ, Wild M, Meyer J, Kasper G. (2005). Filtration efficiency of aerosol particles below 20 nanometers. *Aerosol Science and Technology* 39(8):782-789.
- Hext PM, Tomenson JA, Thompson P. (2005) Titanium dioxide: inhalation toxicology and epidemiology. *Ann Occup Hyg* 49:461-472.
- Hinds, WC, 1999. *Aerosol Technology*. 2nd ed John Wiley & Sons, Inc., New York.
- Hoet PHM, Bröske-Hohlfeld I, Salata OV. (2004) Nanoparticles – known and unknown health risks. *Journal of Nanobiotechnology* 2:12.
- ICON (2006a). http://cohesion.rice.edu/CentersAndInst/ICON/emplibrary/Phase%20I%20Report_UCSB_ICON%20Final.pdf Accessed 2007-06-06
- ICON (2006b) <http://cohesion.rice.edu/CentersAndInst/ICON/emplibrary/ICONNanotechSurveyFullReduced.pdf> Accessed 2007-06-06
- IVA (2006). En nanostrategi för Sverige - ett förslag från IVA (A nanostrategy for Sweden - a proposal from IVA). IVA-M 363, IVA (The Royal Swedish Academy of Sciences), Stockholm.
- Jonas EC, Oliver RM. (1967) Size and shape of montmorillonite crystallites. *Clays Clay Miner.* 15:27–33.
- Karn B, Aguar P (2007) Nanotechnology and Life Cycle Assessment. Synthesis of Results Obtained at a Workshop. Washington DC, 2-3 October 2006. <http://www.nanotechproject.org/111/32007-life-cycle-assessment-essential-to-nanotech-commercial-development>
- Kim S, Harrington M, Pui D. (2007) Experimental study of nanoparticles penetration through commercial filter media. *Journal of Nanoparticle Research* 9(1):117-125.
- Kopstein M. (2006) Potential uses of petrochemical products can result in significant benzene exposures: MSDSs must list benzene as an ingredient. *J Occup Environ Hyg* 3:1-8.
- Kuempel E, Aitken R. (2004) Workshop group G. Regulatory implications. First International Symposium on Occupational Health Implications of Nanomaterials. Buxton, 2004 http://www.hsl.gov.uk/capabilities/nanosymrep_final.pdf#search=%22buxton%20hsl%20niosh%20nano%20%22 Accessed 2006-09-18
- Kuhlbusch TA, Fissan H. (2006) Particle characteristics in the reactor and pelletizing areas of carbon black production. *J Occup Environ Hyg* 3:558–567.
- Kuhlbusch TAJ, Neumann S, Fissan H. (2004) Number size distribution, mass concentration, and particle composition of PM1, PM2.5, and PM10 in bag filling areas of carbon black production. *Journal of Occupational and Environmental Hygiene* 1:660–671.
- Lam CW, James JT, McCluskey R, Arepalli S, Hunter RL. (2006) A review of carbon nanotube toxicity and assessment of potential occupational and environmental health risks. *Crit Rev Toxicol* 36:189-217.
- Lekas D. (2005) Analysis of Nanotechnology from an industrial ecology perspective. Part I: Inventory and evaluation of life cycle assessments of nanotechnologies, revised draft, Yale School of Forestry & Environmental Studies.
- Liden G. (2006) Dustiness testing of materials handled at workplaces. *Ann Occup Hyg*;50:437-439.

- Li P. (2006) Development of Analyses Methodology for Optimum Characterization of Nanoclay and Evaluation of Nano Particle Release from PNC. Diploma work, Dep. Materials and Manufacturing Technology, Chalmers University of Technology, Göteborg.
- Mann S. (2006) Nanotechnology and Construction. Institute of Nanotechnology. <http://www.nanoforum.org/dateien/temp/Nanotech%20and%20Construction%20Nanoforum%20report.pdf-?17072007111038>
- Mark D. (2004) Session 3: Exposure and control issues. First International Symposium on Occupational Health Implications of Nanomaterials. Buxton, 2004 http://www.hsl.gov.uk/capabilities/nanosymrep_final.pdf#search=%22buxton%20hsl%20niosh%20nano%20%22
- Maynard AD, Baron PA, Foley M, Shvedova AA, Kisin ER, Castranova V. (2004) Exposure to carbon nanotube material: aerosol release during the handling of unrefined single-walled carbon nanotube material. *J Toxicol Environ Health A* 67:87-107.
- Maynard AD. (2002) Experimental determination of ultrafine TiO₂ deagglomeration in a surrogate pulmonary surfactant: Preliminary results. *Ann Occup Hyg* 46(Suppl. 1):197-202.
- Maynard AD. (2007) Nanotechnology: The Next Big Thing, or Much Ado about Nothing? *Ann Occup Hyg* 51:1-12.
- Moloney FJ, Collins S, Murphy GM. (2002) Sunscreens: Safety, Efficacy and Appropriate Use. *American Journal of Clinical Dermatology* 3(3):185-191.
- Möhlmann C. (2005) Vorkommen ultrafeiner Aerosole an Arbeitsplätzen. *Gefahrstoffe – Reinhaltung der Luft* 65(11/12):469-471.
- Nanosafe 2 newsletter <http://www.nanosafe.org/node/815>
- NIOSH (2005) Health Hazard Evaluation Report. <http://www.cdc.gov/-niosh/hhe/reports/pdfs/2005-0291-3025.pdf>.
- NIOSH (2007). Progress Toward Safe Nanotechnology in the Workplace. No. 2007-123, NIOSH, Cincinnati <http://www.cdc.gov/niosh/docs/2007-123/pdfs/2007-123.pdf>
- Perez E, Sandgren P. (2007). Nanoteknikens innovationssystem (The Innovation system of nanotechnology). VA 2007:01, VINNOVA (The Swedish Governmental Agency for Innovation Systems), Stockholm.
- Peters G (2004). Risk evaluation & control: Current perspective. Nanomaterials a risk to health at work? First International Symposium on Occupational Health Implications of Nanomaterials. Buxton, 2004 http://www.hsl.gov.uk/capabilities/nanosymrep_final.pdf#search=%22buxton%20hsl%20niosh%20nano%20%22
- Peters TM, Heitbrink WA, Evans DE, Slavin TJ, Maynard AD. (2006) The mapping of fine and ultrafine particle concentrations in an engine machining and assembly facility. *Ann Occup Hyg* 50:249-257.
- Plitzko S, Gierke E, Gernert U. (2006) Syntetische Nanopartikel und Arbeitsplätzen. http://www.baua.de/nn_43190/sid_7468EAEA66E55E01C29EA014515D674B/nsc_true/de/Themen-von-A-Z/Gefahrstoffe/Nanotechnologie/pdf/Vortrag-Plitzko02.pdf See also http://www.baua.de/nn_43190/sid_663CE4A3CB8D08E4118C6371F5A70CD2/nsc_true/de/Themen-von-A-Z/Gefahrstoffe/Nanotechnologie/pdf/Vortrag-Plitzko-03.pdf
- Preining O (1992). The science of ultrafine aerosols. *Pure & Appl Chem* 64(11):1679-1684.
- RIP 3.2 (2005) Technical Guidance Document on preparing the Chemical Safety Report under REACH – Scoping Study – Phase 1 A (REACH Implementation Project 3.2-1A http://ecb.jrc.it/documents/REACH/RIP_FINAL_REPORTS/RIP_3.2-1_CSA-CSR_SCOPING/EXPOSURE_SCENARIOS/RIP3.2-1_WP_1_ES_Final_28072005.doc
- Rosén G. (2002). Seeing is Believing. *Ann Occup Hyg* 46(1):3-4.
- SCENIHR (2006) Modified opinion (after public consultation) on the appropriateness of existing methodologies to assess the potential risks associated with engineered and adventi-

- tious products of nanotechnologies.
http://ec.europa.eu/health/ph_risk/committees/04_scenihr/docs/scenihr_o_003b.pdf
- SCENIHR (2007). Opinion on the appropriateness of the risk assessment methodology in accordance with the technical guidance documents for new and existing substances for assessing the risk of nanomaterials.
http://ec.europa.eu/health/ph_risk/committees/04_scenihr/docs/scenihr_o_004c.pdf
- Schimberg RW, Ukkonen A. (2003) Ultrafeine und feine partikeln in Giessereien (Bronze) und beim Schweissen. BIA_Report 7/2003, pp 163-173. <http://www.hvbg.de/d/-bia/pub/rep/rep04/bia0703.html> Accessed 2006-09-19
- Schneider T, Kildesø J, Breum NO. (1999) A two compartment model for determining the contribution of sources, surface deposition and resuspension to air and surface dust concentration levels in occupied rooms. *Build Environ* 34:583-595.
- Schneider T, Olsen I, Jørgensen O, Laursen B. (1991) Evaluation of exposure information. *Appl Occup Environ Hyg* 6:475-481.
- Schaaf van der D, Heussen H, Wijk van M., Feberle M., Noy D, Tielemans E. (2006) The "Substance Manager", a generic tool for SMEs to control chemical risks at work. Part 1: Background, capabilities and future developments. BOHS Conference 2006, Book of Abstracts.
- Semple SE, Proud LA, Tannahill SN, Tindall ME, Cherrie JW (2001) A training exercise in subjectively estimating inhalation exposures. *Scand J Work Environ Health* 27:395-401.
- Stuer-Lauridsen F, Kamper A, Borling P, Petersen GI, Hansen SF, Baun A. (2007). Kortlægning af produkter der indeholder nanopartikler eller er baseret på nanoteknologi. Kortlægning af kemiske stoffer i forbrugerprodukter Nr 81. Danish Environmental Protection Agency.
<http://www2.mst.dk/Udgiv/publikationer/2007/978-87-7052-468-1/pdf/978-87-7052-468-1.pdf>
- Technical Guidance Document on Risk Assessment, Part 1, 2.2.2.4. (2003)
http://ecb.jrc.it/Documents/TECHNICAL_GUIDANCE_DOCUMENT/EDITION_2/tgdpart1_2ed.pdf
- Thomassen Y, Koch W, Dunkhorst W, Ellingsen DG, Skaugset NP, Jordbekken L, Drabløs A, Weinbruch S (2006) Ultrafine particles at workplaces of a primary aluminium smelter. *J Environ Monit* 8:127-133.
- Tielemans E. (2007) Evaluation of the Stoffenmanager.
http://www.bohsorg/resources/res.aspx/Resource/filename/734/Session-9b_Evaluation_of_the_Stoffenmanager_Eric_Tielemans_TNO.pdf
- Tielemans E, Warren N, Schneider T, Tischer M, Ritchie P, Goede H, Kromhout H van Hemmen J, Cherrie J. Tools for regulatory assessment of occupational exposure: -development and challenges. *Journal of Exposure Science and Environmental Epidemiology*. Accepted.
- Ukkonen A, Lamminen E, Kasurinen H. (2005) Measuring the size distribution and concentration of particles formed in plasma arc cutting. NOSA Aerosol Symposium, Göteborg, Sweden 2005.
<http://www.fysik.lth.se/eriksw/NOSA2005/nosa2005proceedings.pdf>
- Wake D, Mark D, Northage C. (2002) Ultrafine aerosols at the workplace. *Ann Occup Hyg* 46(Suppl 1):235-238.
- Welsh MS, Lamesse M, Karpinski E. (2000) The verification of hazardous ingredients disclosures in selected material safety data sheets. *Appl Occup Environ Hyg* 15:409-20.
- Woodrow Wilson International Center for Scholars (2007) A nanotechnological consumer products inventory.
<http://www.nanotechproject.org/index.php?id=44&action=intro> . Accessed June 2007

Resume

Anvendelse af tekniske nanopartikler byder på store økonomiske og tekniske muligheder. Nogle af disse muligheder skyldes partiklernes specielle egenskaber, herunder at de kan fremstilles med særlige reaktive egenskaber. På grund af de mulige sundhedsrisici forbundet hermed har forskere, administratorer og industrien igangsat initiativer for at fremskaffe viden om arbejdsbetinget eksponering og at fastlægge, hvad der er sikker brug af de forskellige tekniske nanopartikler.

Rapporten giver et generelt overblik over nanopartikler og hvordan de fremstilles og anvendes i industrien i de nordiske lande. Der skelnes mellem

- Tekniske nanopartikler, dvs. partikler der har en diameter på mellem 1 og 100 nm og som er fremstillet med det formål at give dem specifikke egenskaber som form, størrelse, overfladeegenskaber og kemiske egenskaber.
- Ultrafine partikler, et udtryk der har været brugt til at beskrive luftbårne partikler som er mindre end 100 nm. Betegnelsen “ultrafine” har været i brug længere end “nano”. Betegnelsen “ultrafine” bruges ofte for partikler der er opstået som (uønsket) biprodukt ved fx forbrænding og svejsning. Også flere partikler fremstillet med vilje med størrelse i nanoområdet (fx carbon black, silicarøg, og titandioxid TiO_2) benævnes ofte “ultrafine”.

Flere materialeteknologier involverer processer som transformere konventionelle materialer til partikler i nanostørrelse. Fx anvender termisk overfladecoating med plasmaspray nanopartikler for at opnå en coating med nanoegenskaber. Høje koncentrationer af partikler af nanostørrelse dannes også som biprodukt ved konventionelle processer hvor der indgår fordampning/kondensation.

Tekniske nanopartikler omfatter metalliske og keramiske nanopartikler, fullerener, en af de mest kendte nanopartikler, nanorør, hvor de mest kendte er nanorør af kulstof, nanofibre, nanoler, nanokapsler, dendrimerer og kvanteprikker.

Nogle eksempler på forskning, fremstilling og anvendelse af nanopartikler præsenteres for hvert af de nordiske lande.

Både partiklernes størrelsesfordeling og deres tilbøjelighed til at afgive støv når de håndteres er vigtige data for en risikovurdering, både for eksisterende og nye stoffer. Annex V af Dir 67/548/EEC dækker endnu ikke i tilstrækkelig grad over dette testbehov. I mangel af formelle krav har projektgruppen foreslået, at et første trin i en karakterisering bør om-

fatte partikelstørrelse, form, agglomereringstilstand, specifikke overfladeareal, krystallinitet samt grundstofsammensætning. Tre pulverprøver blev karakteriseret efter dette skema.:

- Ikke-coatet titan dioxid pigment (anatas)
- Aluminium behandlet ultrafin titan dioxid (rutil)
- Tør silica røg

Som eksempel blev der fundet følgende specifikke overflade arealer: $5.5 \text{ m}^2 \text{ g}^{-1}$ for titandioxid pigment, $112 \text{ m}^2 \text{ g}^{-1}$ for ultrafin titan dioxid og $12 \text{ m}^2 \text{ g}^{-1}$ for silicarøg.

De få støvningstest der er publiceret viser at håndtering af nanopulver har en tilbøjelighed til at afgive partikler der har en størrelsesmode under $1 \mu\text{m}$, typisk $100\text{--}300 \text{ nm}$, samt en eller flere modes over $1 \mu\text{m}$. Håndtering af kulstof nanorør pulver har vist sig at kun at resultere i lave antalskoncentrationer.

For at kunne udforske støvningsegenskaberne yderligere blev en ny støvningstest udviklet. Den bruger kun lidt materiale og kan på en enkel måde bygge bro mellem de to forskellige testprincipper der er specificeret i EN 15051 standarden for støvningstest. Støvningstest blev udført for ultrafin og pigment grade TiO_2 , silica røg, bentonite, yttrium stabiliseret zirconia, goethit, to finhedsgrader af korund (aloxite F800 og F1200), samt talk. Alle materialer dannede støv, der havde to størrelsesmodes over $0.9 \mu\text{m}$. Alle materialer, med undtagelse af pigment grade TiO_2 og aloxite F1200, havde også en størrelsesmode i området fra ~ 100 til $\sim 220 \text{ nm}$. TiO_2 pigment grade støvede mindst og TiO_2 ultrafin mest af alle undersøgte materialer. Forskellen var en faktor ~ 300 . En tilsvarende forskel i eksponeringspotentiale kan forventes. Det betyder, at de forebyggende foranstaltninger må gøres meget strengere hvis pigment grade TiO_2 erstattes med den ultrafine version. Siden aggregater af ultrafin TiO_2 kan brydes i lungevæskerne og under antagelse af, at partikelantal er en risikofaktor, vil forøgelsen af den potentielle risiko blive endnu større. Resultaterne viste, at når man håndterer nanopulver, vil de dannede luftbårne partikler være agglomerater, ikke enkelte primære nanopartikler.

Der er for lidt viden om risici til at kunne specificere hvilket kontrolniveau der kræves og dermed at kunne vejlede om valg af egnede kontrolforanstaltninger. Der er udviklet flere fremgangsmåder for konventionelle materialer og de kan udgøre et begrebsapparat til beskrivelse og analyse af eksponeringsscenarier for nanomaterialer. Til dem hører ”control banding” og eksponeringsmodellering. Disse begreber beskrives. Projektgruppen er af den opfattelse at metoder til teknisk kontrol af eksponering for nanopartikler kan bygge på viden og erfaring fra eksponeringskontrol for konventionelle partikler. Det bør bemærkes, at der allerede i dag anvendes tekniske foranstaltninger til kontrol af eksponering for ultrafine partikler som fx svejserøg, carbon black og vira. Effektive

metoder kan opnås ved at tilpasse og omdesigne eksisterende teknologi. Det vedrører teknikker for almen ventilation, industriel ventilation, lokal- og procesudsugning, indkapsling og filtrering.

Også arbejds-hygieniske vurderinger af arbejdspladser kan følge eksisterende metoder. En undtagelse er, at selv ekstremt høje koncentrationer af nanopartikler ikke nødvendigvis er synlige for det blotte øje. Derfor vil anvendelse af tilstrækkeligt følsomme måleinstrumenter for nanopartikler som fx kondensation partikeltæller komme på tale.

Der findes endnu ingen nationale eller internationale standarder for målemetoder for nanopartikler på arbejdspladser. Dette har begrænset omfanget af eksponeringsmålinger, hvorfor der kun findes et meget begrænset antal eksponeringsdata. Måling af eksponering for nanopartikler byder på nogle store udfordringer:

- Eksponeringen vil oftest være i form af aggregater. Der findes ingen simple målemetoder til bestemmelse af agglomereringsgrad og i hvilken grad de brydes op i mange flere mindre enheder i lungevæsken efter deponering i luftvejene.
- Der er på de fleste arbejdspladser en høj baggrundskoncentration af partikler i nanostørrelse. I dag findes kun to feltmetoder til at skelne baggrund fra tekniske nanopartikler i samme størrelsesområde. Den ene er intelligent designet målestrategi. Den anden er at opsamle partiklerne på et passende substrat for efterfølgende laboratorieanalyse med tidskrævende elektronmikroskopi.

For at sætte eksponering for tekniske nanopartikler i perspektiv præsenteres udvalgte eksponeringsscenarier for ultrafine partikler. Koncentrationen målt i antal partikler var fra over 10 000 000 partikler cm^{-3} for laser-svejsning til koncentrationer på omkring 1 000 til 10 000 partikler cm^{-3} for afsækning af ultrafine pulvere.

Et af projektets formål var at indsamle eksempler på specifikke scenarier for eksponering for tekniske nanopartikler. Det måtte konstateres, at der kun var få scenarier tilgængelige for nærmere undersøgelse. Denne erfaring deles med kolleger i andre europæiske lande. De data, der kan præsenteres, er derfor af meget varierende detaljeringsgrad og omfang. Det er derfor heller ikke muligt at drage almene konklusioner om eksponeringsrisiko.

På grund af disse begrænsede data var det ikke meningsfuldt at forsøge at vurdere sandsynlighed og intensitet for arbejdsbetinget eksponering for tekniske nanopartikler i hele livscyklus forløb.

Kvaliteten af den information, der gives i sikkerhedsdatablade (SDS), blev undersøgt. Der blev udvalgt materialer med primær partikelstørrelse så lille som mulig, og for at afspejle en bred vifte af egenskaber. Materialerne kom fra følgende stofgrupper (antal i parentes): silica (8), titandio-

xid (4), zircondioxid (2), kulstof nanorør (11), C₆₀ fullerener (2) og cadmium-baserede kvanteprikker (3).

Generelt var identifikation af stoffet og af virksomheden tilfredsstillende. Inden for stofgrupperne var opregning af R-sætninger inkonsistent. I mange tilfælde manglede angivelse af klassificering og mærkning i SDS, fordi der ikke fandtes testresultater. I nogle tilfælde var "nano" anført i materialets kommercielle navn. De fleste af kulstof nanorør materialerne var identificeret som grafit.

Kvaliteten af de foreslåede forskrifter for håndtering, opbevaring og eksponeringskontrol varierede meget mellem de forskellige SDS, selv for materialer af samme karakter. Også beskrivelsen af de fysiske og kemiske egenskaber samt forhold, der skulle undgås, var meget forskellig for de forskellige SDS. Nogle SDS havde en velbeskrevet liste af grænseværdier og toksicitetstest. Imidlertid varierede beskrivelsen af de toksiske egenskaber selv for sammenlignelige stoffer. Der var meget lidt information om økologiske forhold i SDS.

Generelt blev stofferne/materialerne så godt som ikke testet, og hvis de blev, så var det kun for akut toksicitet.

Afslutningsvis anføres nogle betragtninger om den nærmeste tids udviklingstendenser for produktion og anvendelse af tekniske nanopartikler.